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FINAL REPORT

"FURTHER FEASIBILITY STUDY ON THE USE OF FTIR
(FOURIER TRANSFORM INFRARED) TO QUANTIFY THE DEGREE OF OXIDATION OF COAL"

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ABSTRACT

Fourier Transform Infrared Spectroscopy (FTIR) with conventional thermoelectric detection or with photoacoustic detection (PAS-FTIR) has been used to examine the extent of oxidation of a series of western bituminous coals subject to differing extents of natural weathering (as estimated by depth from the surface of a seam). The samples of coals were subjected to quantitative demineralizations by acid treatment and to quantitative derivatizations by phase-transfer methylations of all acidic hydroxy functions.

The derivatization and demineralization procedures were also applied to series of samples of British Columbian and Nova Scotian bituminous coals which had been subjected to artificial aerial oxidation at temperatures ranging from 100 to 150 degrees C for varying periods. Detailed experimental descriptions are provided for these manipulations.

The specific nature of the major components of the introduced oxygen functionality in the most extensively oxidized of the naturally weathered coal samples were identified as aromatically and aliphatically linked carboxylic acids by a process of selective methylation, yielding the corresponding methyl esters, which show individually distinct carbonyl absorptions.

Alkaline hydrolysis followed by reacidification reverses these changes. Other carbonyl functionality (probably aromatic-aliphatic ketones of various types) is present but is never the major component of the total infrared signal above 1650 cm^{-1} .

In the naturally weathered samples, significant proportions of the carboxylic acid functionality have been converted in situ into carboxylate

salts, and in order to derive meaningful indications of the true carboxylic acid content, preliminary demineralization of the coal is necessary. Detailed comparisons of conventional FTIR spectra (obtained using the potassium halide pellet technique) and the photoacoustic infrared spectra (where the sample in effect acts as its own detector) were made for a large number of the coals and the derivatization/demineralization products. The reproducibility and comparability of series of spectra obtained for sequence of samples using both techniques were studied, and we conclude that with appropriate precautions, the photoacoustic technique offers all the information provided by conventional FTIR, without the chore of sample preparation. Internal self-scaling by matching intensities of a standard peak enables pseudo-three-dimensional plots of spectral changes in the coals as functions of oxidation time or depth within a seam to be presented in straightforward display format.

INTRODUCTION AND REVIEW

It has been known for many years that bituminous coals absorb oxygen slowly at ambient temperatures (below 40 degrees celsius) and rapidly at high temperatures (above 150 degrees celsius), altering swelling and caking characteristics (such as free-swelling indices, fluidities, and dilatations). The presence of oxidized coal in a coking blend may adversely affect coking properties and coke quality (1), although suppression of caking by oxidation can be an advantage if a strongly swelling coal is to be used for gasification or combustion (2). It has been reported recently (3) that some Western Canadian bituminous coals yield considerable amounts of unburnt carbon in the fly-ash residue under conventional burner technology; this behavior has been attributed to in situ oxidation of vitrinite, which persists through the burner flame in a partially reacted form. Since a large proportion of the Western Canadian coals of potential use for thermal energy generation are weathered or oxidized to some extent, prediction of likely combustion behavior, and development of alternative combustion procedures, are high priorities. Identification of the nature of the oxygen functionality in oxidized coals is a key first step towards elucidation of the reasons underlying the losses of swelling properties and the inefficiencies of combustion of such coals, and the eventual development of technologies correcting or compensating for the loss of desirable properties.

However, despite the evident technological significance of the oxidation/weathering processes, their courses are poorly understood. Such critical points as the chemical nature, rate, and mechanism (or mechanisms)

of the oxidation reactions, and their dependence upon temperature, and their variability (or constancy) between different coal types, and the relationships between the extent and nature of oxidation and changes in combustion and swelling behavior, remain unresolved.

The Problem of Identification of Introduced Oxygen in Bituminous Coals

To a neophyte in coal chemistry, it would appear that direct physical identification of newly introduced oxygen functionality in the coal, or quantitative derivatization and/or conversion, should allow elucidation of oxidation pathways. For example, infrared spectroscopy might be expected to be useful for the physical identification, but in practice has not achieved results commensurate with its apparent potential. Indeed, after an initial flurry of activity over twenty years ago, little new information has been provided by this technique until very recently. Difficulties arise because coals are highly absorbing, and without lengthy sample preparation it is not practicable to obtain high-quality spectra with conventional (dispersive) infrared instrumentation. Effective distribution of a coal sample in the standard potassium halide matrix often employs extensive grinding, and such processing can result in further adventitious oxidation. Also, overlap and superposition of many bands arising from slightly different environments for similar functional groups results in spectra consisting of poorly resolved bands with little fine structure, allowing only very general and qualitative, non-definitive, identification or a few functional groups. Detection of small proportions of new or added oxygen functionality

is very difficult. Enhancement of sensitivity by quantitative derivatization of functional groups is limited because of the uncertainties about quantitative conversion of coals (mass transport factors such as reactant insolubility and reagent inaccessibility are responsible), and again detection of small proportions of added functionality is difficult.

Recent work using computerized Fourier Transform Infrared (FTIR) instruments has gone some way towards more precise characterization (4-6). Such instruments possess a number of advantages compared to dispersive instruments (see Griffiths (7) and Koenig (8): The use of an interferometer rather than a system of gratings and slits gives much higher energy throughput at the sample and the detector, and the internally calibrated computerized system can co-add a large number of interferograms. In addition, the pulsed operation where all frequencies are covered in each scan greatly accelerates data acquisition.

In favorable cases, the course of a reaction of a complex polymer (such as a coal undergoing oxidation) may be followed by computer-controlled subtraction of the Fourier-transformed interferograms recorded sequentially for different stages of oxidation, using identical sample preparation procedures. However, significant difficulties remain in ensuring comparability of the actual spectra if the potassium halide pellet technique is used. The ubiquitous presence of water associated with the coal in the halide matrix, even if great care is taken, makes spectral subtraction of doubtful accuracy in regions where hydrogen-oxygen stretching and deformation vibrations are present.

Previous Studies of Oxidized-Weathered coals using Infrared Spectroscopy
and/or Chemical Derivatization: The Diversity of Opinion

In this section of the report, a summary presentation of previous work is given to indicate the current lack of consensus about the added functionality in oxidized coals.

Over twenty years ago, Durie and his co-workers (9) studied the oxidation of an Australian vitrain carried out at 170 and at 190 degrees celsius, and concluded that the important changes were the virtual disappearance of aliphatic structures and the appearance of aromatic carboxylic acid groups. In one of the most recent publications on this topic, Painter and his co-workers (5) conclude that oxidation of PSOC337 bituminous coal at 150 degrees generates carboxylate (CO_2^-) and carbonyl (probably aryl alkyl ketonic) groups at the expense of methylene groups. In contrast, Berkowitz and his colleagues at the Alberta Research Council (10) report that aerial oxidation of Western Canadian bituminous coals leads to ketonic forms, with virtually no increase in acidic oxygen-containing groups, and Nandi, Montgomery and their co-workers (11) report that the carbonyl content (i.e. ketonic or quinonoid function) of Balmer 10 low-volatile bituminous coal remained the same after oxidation at 100 degrees for 3 days, and no carboxylic acidity was detectable; this brief oxidation was sufficient to eliminate the swelling properties of the coal, and it was suggested that the additional oxygen was in the form of ether groups.

DeVries, Bokhoven, and Dormans (12) found increases in acidic hydroxyl, carboxylic acid groups, and ketonic carbonyl accompanying oxidations of two bituminous coals at 100 degrees, while Albers, Lenart, and Oerlert (13) found

increases in carbonyl (assumed quinonoid) content and in non-reactive oxygen with little change in hydroxyl groups, for oxidation of two bituminous coals at 129 and at 148 degrees.

More recently, Bouwman and Freriks (14) concluded from an FTIR study of samples from a coal pile that carboxylic acid groups are generated as a consequence of spontaneous heating of piles, while Liotta and his co-workers at Exxon Research (15,16) find, similarly using FTIR spectroscopy, that there are substantial increases in absorption in the 1100 cm^{-1} region for samples of air-weathered Illinois bituminous coals as compared with the fresh coal, and they suggest that the increased absorption results from the generation of new ether linkages.

The situation reveals no consensus and may be summarized as one of the almost total confusion and disagreement; this may be explained fairly readily since most assertions concerning the presence or generation of specific new oxygen functionality are based either upon the generation of a new infrared peak assignable to one or the other of a ketone or a carboxylic acid group (as holds for the work of Painter and co-workers (4-6), Albers and co-workers (13), and Bouwman and Freriks (14)), or are based upon chemical derivatizations or conversion reactions (such as "ether cleavage") of unproven specificity and quantitation. The very early study by Durie and co-workers (9) is unique in that the presence of carboxylic acid functionality in their oxidized vitrains was proved by ion-exchange conversion into carboxylate ions, showing that this treatment removed virtually all the 1700 cm^{-1} absorption. However, instrumental limitations of sensitivity and resolution made it impossible for them to detect changes at early oxidation stages.

Method and Experimental Procedures for Resolution of the Nature of Carbonyl
Functionality in Artificially and Naturally Oxidized Coals.

The feature of added carbonyl-type oxygen group absorptions in the infrared spectra of the oxidized coals as a broad peak in the 1650-1750 cm^{-1} region may be enhanced by spectral subtraction routines (compare Painter and co-workers (4-6)), but in the absence of chemical derivatization conversion procedures applied to the oxidized coal in order to establish the specific nature of these carbonyl groups and their intrinsic intensities, the enhancement procedure proves little.

We have sought to resolve this key question as follows: as a first step, we effect quantitative derivatization of the coal samples by an alkylation process based upon a simplified version of that reported recently by Liotta and co-workers (17,18). In this process, coals, swelled in aqueous tetrahydrofuran suspension, are reacted with a tetraalkylammonium hydroxide to form coal anions, which are then reacted further in a simple bimolecular nucleophilic displacement reaction with an alkyl halide (generally, methyl iodide is used, resulting in methylation of the coal). This procedure converts all acidic hydroxyl groups (phenolic and carboxylic acid) into methylated functions. The effect of methylation is to narrow the frequency range over which a particular type of carbonyl group shows an infrared peak, while extending the general frequency region in which the carbonyl peaks appear. In particular, the intermolecular association of carboxylic acid groups is suppressed and instead of being localized in the 1700 cm^{-1} region, or immersed in the main envelope of the "1600 cm^{-1} band", absorptions are

sharpened and shifted to higher frequencies, with methyl esters of aliphatic-type carboxylic groups having peaks around 1735 cm^{-1} , and methyl esters of aromatic-type carboxylic groups having peaks from $1715\text{--}1720\text{ cm}^{-1}$. The observations of these separations were first used over twenty years ago in an infrared study of modified Australian lignites (brown coals) and lignins (Lynch, Durie, and co-workers (19,20)). Also the completely methylated oxidized coals may be subjected to selective hydrolysis of the methoxycarbonyl components, thus reversing the changes observed in the 1700 cm^{-1} region, and providing additional confirmatory evidence of the nature of the carbonyl-type functions. Studies with model hydroxyaryl-substituted aryl alkyl ketones (such as hydroxytetralones) show that analogous shifts of the carbonyl peaks to higher frequency occur accompanying hydroxy-to-methoxy conversion, but these changes are not reversed by the conditions leading to hydrolysis of the methoxycarbonyl functions.

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APPENDIX 1

QUANTITATIVE METHYLATION (A MODIFICATION OF THE PROCEDURE OF R. L. LIOTTA, FUEL, 58, 724 (1979)):

One gram of the powdered coal (-200 mesh) is stirred under nitrogen for 2 h. in 40% aqueous tetrabutylammonium hydroxide (10 ml.) and tetrahydrofuran (10 ml.). Iodomethane (2.0 ml.) is added and mixture stirred overnight in a stoppered, sealed, flask under a nitrogen atmosphere.

The methylated product is diluted with methanol (100 ml.) and the product collected by suction filtration, and exhaustively extracted in a soxhlet apparatus with methanol (300 ml.) until the extract is free of iodine ion (6-12 hours extraction). The solid residue (the methylated coal) is washed thoroughly by suction on a sintered-glass filter using methanol as wash liquid, air-dried, and dried under vacuum at 100 degrees in a drying pistol. The dried product is stored in screw-cap vials.

DEMINERALIZATION PROCEDURE (based on a procedure used for Australian coals by H. R. Brown, R. A. Durie, and H. N. S. Schafer, Fuel, 38, 295-308 (1959)):

Two grams of the powdered coal (-200 mesh) are heated in refluxing 5M aqueous hydrochloric acid for 1 h. After cooling, the coal sample is collected by suction filtration, and immersed in 25% aqueous hydrofluoric acid (100 ml.) at 50-55 degrees (water bath) for 1 h. The coal sample is suction-filtered, washed with water (1 litre), and heated under reflux for a further hour with 5M aqueous hydrochloric acid. The demineralized product is treated by soxhlet extraction with water until the extract is free of chloride ion. The solid residue is dried in a nitrogen stream and further dried under vacuum at 100 degrees. Samples are stored in screw-cap vials.

EXPERIMENTAL PROCEDURES

General

A summarizing set of examples of the coal samples examined by FTIR and PAS-FTIR is listed in the Index to Spectra, and displayed in Figures 1 through 35, following the main body of the Report. The set is limited in scope and is illustrative, not exhaustive, since over four hundred spectra were obtained for the series of samples studied, which include coals, derivatization of purification products, and model compounds. The complete data base of all spectra is in permanent storage in digitized form and will continue to be available for recall, expansion and emphasis of features, correction and subtraction procedures, and cross-correlation analyses.

Instrumentation

Spectra were obtained using the Bruker IFS110 Infrared Fourier Transform Spectrometer located in the Chemistry Department Instrumentation Centre, St. Francis Xavier University. Standard KCl pellet spectra were obtained using a deuterated triglycine sulfate detector, and the photoacoustic spectra were acquired using the E G & G Princeton Applied Research Model 6001-6003 photoacoustic cell/amplifier system coupled to the IFS110.

Sample Preparation

For the potassium chloride pellet spectra, approximately 3-5 mg of sample and 300-500 mg of high-purity potassium chloride were ground in a Crescent Wig-L-Bug for 8 min and were converted by application of pressure (approximately 5000 Kg for 2 min) with simultaneous evacuation into 13 mm diameter pellets of about 120-150 mg.

For the photoacoustic spectra, about 50 mg of sample was placed directly into the cell cavity.

Provenance of Oxidized Coals

Series of artificially oxidized Cape Breton coals available from a previous study (DSS File No. 20 SU 23440-9-9047/2) were used as precursor material for further chemical conversions. Some artificial oxidations were also performed using the Western depth-profiled samples supplied specifically for this study. The general conditions for oxidations were similar to those used by us previously, and they are specifically identified in descriptions of the Figures of spectra.

Data Acquisition and Presentation

32 interferograms were co-added for the conventional FTIR spectra (KCl pellets), and 128 for the photoacoustic spectra, using specified resolutions of 4 cm^{-1} . For the photoacoustic spectra, the transmission reference at each frequency is the transmission of a standard carbon black (black-body) sample. The interferograms were Fourier transformed and stored on high-density hard disk in the forms of frequency spectra covering the range $4000\text{--}400\text{ cm}^{-1}$. The displayed spectra in Figures 1 through 35 represent selected segments of the complete data sets and have been smoothed digitally by averaging intensities at frequencies above and below a specific fiduciary data point/frequency address. In examples where multiple spectra are displayed on a single Figure, the spectra are scaled for constant intensity of the most intense peak in the spectral region displayed, and sequential plots are displaced vertically by constant amounts in order to enhance perception of progressive changes.

DETAILED COMMENTARY ON FIGURES OF SPECTRA (see INDEX OF SPECTRA, and FIGURES 1 through 35)

(Figures 1-9 are standard spectra; Figures 11 through 35 are photoacoustic FTIR)

Figure 1

Illustrates the enhancement of the carbonyl peak intensity by the methylation process by comparison of the spectra of the highly weathered coal W-4 before and after methylation, and also shows the shift to higher frequency. Note also a shoulder in the 1650 cm^{-1} region and the asymmetry of the peak centered at 1720 cm^{-1} .

Figure 2

Illustrates the effect of acid-washing on a weathered coal, converting carboxylate into carboxylic acid groups. Note that assessment of carbonyl content in the as-received coal from the peak intensity would be highly unreliable.

Figure 3

Illustrates that the high-frequency shift and intensity enhancement accompanying methylation is still evident in a comparison between the washed coal and the methylation product. The extent may be exaggerated by the presentation mode because the intrinsic intensity of the " 1600 cm^{-1} band" is used as the scaling basis and the methylation decreases the intensity of this band on a weight-factor basis.

Figure 4

Illustrates methylation effects as a function of depth-in-seam for three samples in the W-series.

Figure 5

Illustrates that most of the carbonyl component in the extensively weathered coal W-4 is carboxylic acid type (alkaline hydrolysis of the

methoxycarbonyl groups, converting them to carboxylate, virtually eliminates absorption in the 1700 cm^{-1} region. This change is reversed by re-acidification (Plot 3). Note that the relative intensity differences between the carbonyl absorptions in plots 3 and 4 result from the weight-factor difference accompanying etherification of phenolic hydroxyls.

Figure 6

Illustrates similar effects to Figure 5 with another sample of heavily weathered coal; note that bicarbonate treatment virtually eliminates carboxylic acid absorptions. Note also that the methoxycarbonyl band in this spectrum is significantly broader than for the purportedly identical W-4 in Figures 1 and 2 (maceral variations within an identical sample?).

Figure 7

Illustrates the progressive changes in methoxycarbonyl peak absorption as a function of time of oxidation for Cape Breton Coal #1. Note that the coals are oxidized, then methylated subsequently.

Figure 8

Similar illustration for Cape Breton Coal #4, where the Liotta methylation procedure was used (contrast the diazomethane-effected methylation for the previous set).

Figure 9

Similar illustration for Western Coal #5. Note that the artificial oxidation of this coal is not giving the same behavior as the Cape Breton coals. Possibly the carbonyl species is ketonic, as suggested by Berkowitz.

Figure 10 is omitted (it duplicates Figure 7)

Figure 11

Illustrates effects of methylation of the weathered coal W-4 in the C-H stretch region; as expected, the introduction of methoxy groups increases absorption, particularly in the 2900-2800 cm^{-1} region.

Figure 12

Illustrates the effects of methylation of the deepest sample of the W series (W-16) in the same region as Figure 11. Methylation effects are less marked.

Figure 13

Illustrates the changes between the as-received and demineralized samples of W-4. Note the marked increase in the 1700 cm^{-1} region absorption and the decreased intensity of the 1600 cm^{-1} band.

Figure 14

Similar illustration, focussing on the removal of S-O or Si-O species from the coal as a consequence of demineralization.

Figure 15

Demonstrates marked differences in the intensities of C-H absorptions when comparing the unweathered coal (W-16) and the weathered coal (W-4) from the same seam.

Figure 16

Similar comparisons of W-16 and W-33 in the carbonyl-stretch region.

Figure 17

Further illustration of differentially increased absorption intensity in the C-O stretch regions accompanying methylation of W-4 as compared to W-16 (compare Figures 11, 12).

Figure 18

Illustration of additional fine structure in the C-H stretch region for W-4 by comparison of pre- and post-methylation spectra.

Figure 19

Illustration of variability between spectra of samples (purportedly identical, but not duplicates).

Figure 20

Complete sequence of effects of time of oxidation for Cape Breton coal #4, as revealed after methylation of the oxidized coal samples. Note progressive shift of the carbonyl-type absorptions to higher frequencies, and resolution of separated absorptions (contrast Figure 8).

Figure 21

Similar sequence for Western coal #5. Contrast with coal #4 for the relative intensities of the peaks above 1680 cm^{-1} .

Figure 22

Comparison of the methylated coals from W-16, W-4, and artificially oxidized and methylated W-16. Shows that the functional groups are essentially the same for plots 2 and 3.

Figure 23

Sequential changes in double-bond stretch regions with time of oxidation for diazomethane-methylated Cape Breton coal #2.

Figure 24

Same pattern of behavior for Cape Breton coal #3 subjected to methylation by diazomethane after oxidation.

Figure 25

Comparisons of methylated samples for various depths in the W series. plots 2 and 3 show reproducibility of spectra for processing of separate samples of identical coals.

Figures 26, 27

Further comparisons using W-16 (methylated) as base species.

Figures 28, 29, 30

Progressive changes in the carbonyl-stretch region for methylated samples from high-temperature oxidations of W-4 for varying times.

Figures 31, 32, 33

Progressive changes in the carbonyl-stretch region for methylated samples from high-temperature oxidations of coal W-16 for varying times.

Note the general similarity of the final oxidation stage with methylated W-4.

Figure 34

Effects of intense infrared irradiation at 85° of coal W-16 on absorptions in the C-H stretch regions. Note that unlike high-temperature oxidations, there is a relative loss in aromatic absorptions.

Figure 35

Similar samples, focussing on changes in the C-O stretch region. The progressive loss of fine structure could be due to C-O-O-C (endoperoxide) formation and/or some thermal decomposition of these species to ethers.

ASSESSMENT OF WEATHERING (NATURAL OXIDATION) OF THE SERIES OF COALS
W-1 THROUGH W-16

We have used the approach of ratioing the intensities of the carbonyl-type peaks at and above 1700 cm^{-1} to the intensity of the 1600 cm^{-1} region absorption in the quantitatively methylated coal samples to establish the following orders for the extent of oxidation, which follow almost perfectly the depth of the sample from the surface. In view of the facts that the sampling process were random ones, and we were not advised until measurements were complete that the sixteen samples represented only eight differing entities, some of which are separated by only 50 cm in depth profile, this success is remarkable. The order based simply upon the "1700/1600" baseline intensity ratio, expressed in percentage form, is reproduced in the Table:

TABLE
Deduced Orders of Oxidation in Methylated Coals

Sample #s	Percentages	Depth in Seam (m)
1, 4	41, 40	6
2, 9	38, 37	24
5, 10	27, 31	27
6, 13	30, 30	28
11, 15	30, 44(?)	28.5
8, 14	25, 25	29
3, 12	19, 24	29.5
7, 16	29(?), 10	33

Similar patterns are shown if more of the discrete peaks above 1700 cm^{-1} are incorporated into the ratioing, but the results from the simple analysis above are difficult to better.

CONCLUSION

It is evident that photoacoustic infrared spectroscopy provides a rapid method of assessment of the oxidation levels of bituminous coal samples, either naturally weathered (compare previous section) or artificially oxidized (compare Figures 20 through 24). Quantification may be achieved readily by cross-correlation with detailed ultimate analytical data for sets of demineralized, quantitatively methylated coals. Analyses of oxidized coals on a service basis should be readily attainable given appropriate instrumentation combined with careful derivatization procedures (see Appendix 1).

ACKNOWLEDGEMENTS

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INDEX OF FTIR AND PAS-FTIR SPECTRA

SAMPLE DESIGNATIONS

Bituminous Coals:

1. Cape Breton Development Corporation # 26 Mine, washed sample.
2. Cape Breton Development Corporation, Langan Mine, washed sample.
3. Cape Breton Development Corporation, Prince Mine, washed sample.
4. Cape Breton Development Corporation, Langan Mine, washed sample.
- 5, 6. Western Research Laboratory, E. M. & R. Western coal, as received.

W-1 through W-16: Depth-profiled samples provided by Western Research Laboratory, E. M. & R.

Sample Pre-Treatments:

Coals 1-4 were ground to -200 mesh at the Nova Scotia Research Foundation, Dartmouth, N. S. and were stored in sealed containers at 20 degrees C.

Coals 5 and 6 were ground to approximately -60 mesh in a Brinkmann pulverizer system and stored as above.

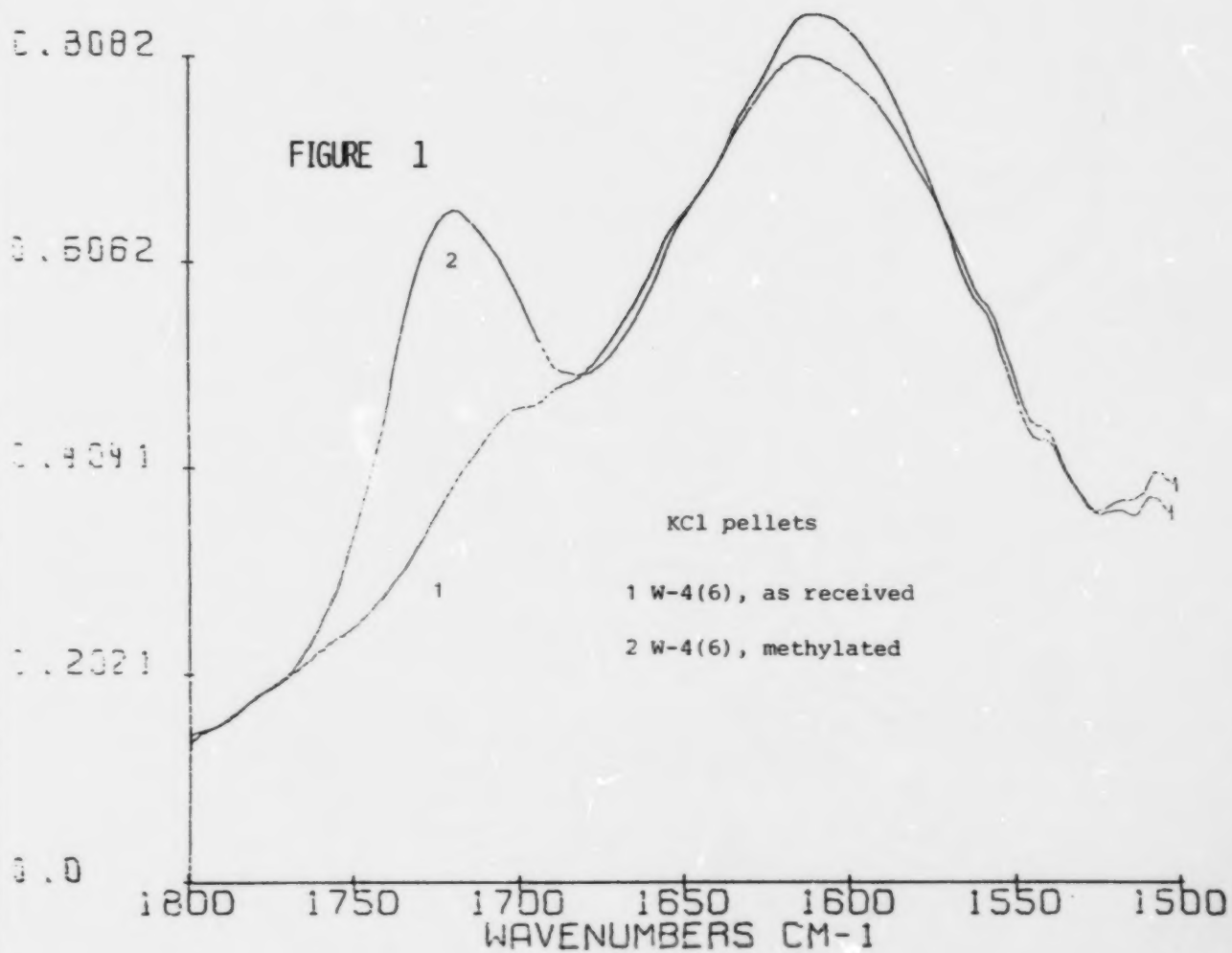
Coals W-1 through W-16 were ground similarly to -200 mesh and stored in lock-sealed polythene bags under nitrogen. Samples are coded by depths in parentheses following sample #'s.

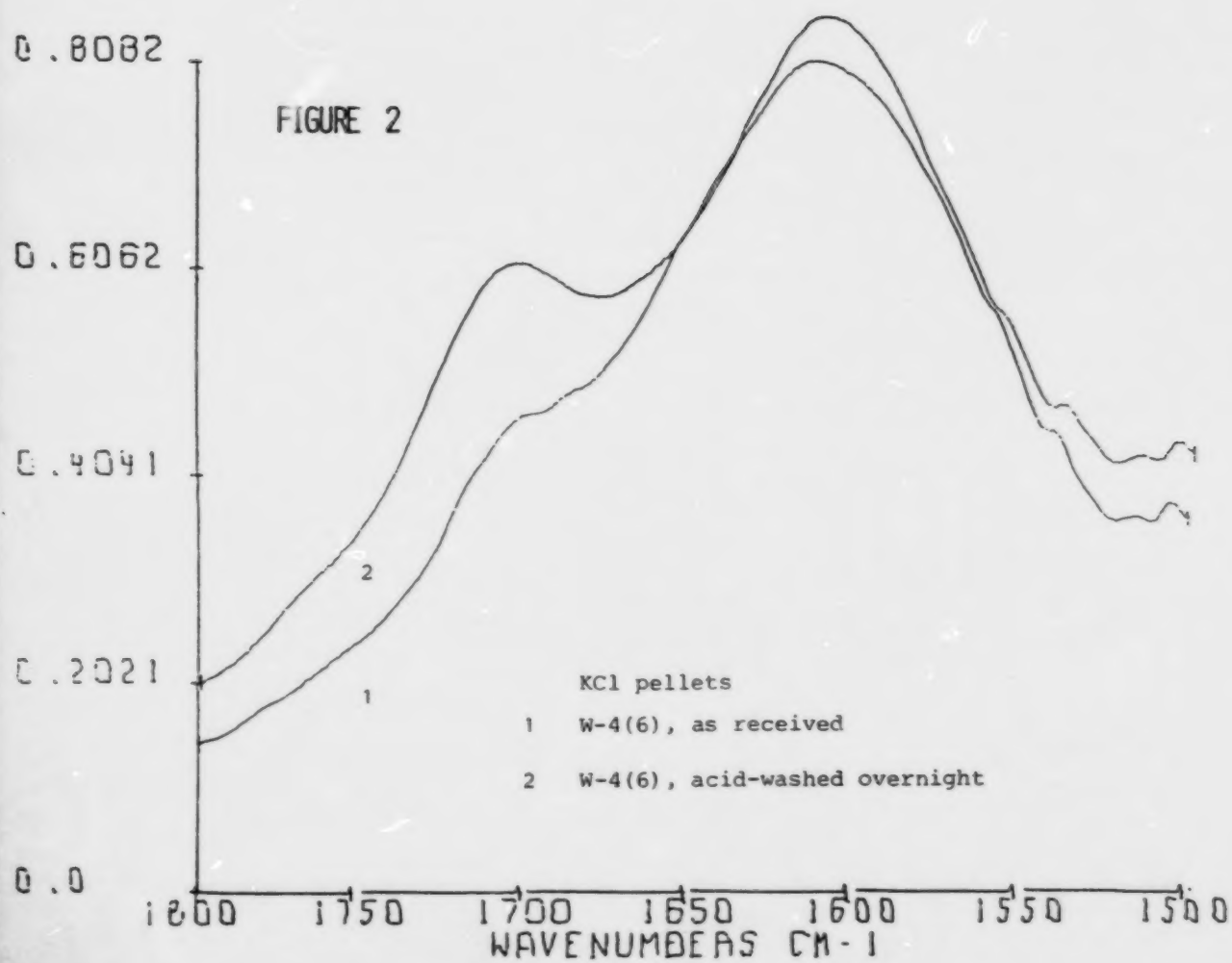
For artificially oxidized coals, sample treatment is identified by coal # - hours of oxidation - temperature of oxidation. e.g. 5 - 100 - 122.

<u>Fig. #</u>	<u>Type</u>	<u>Sample Description</u>	<u>Frequency range (cm⁻¹)</u>
(Unless indicated otherwise, all spectra are acquired in photoacoustic mode. "KCl" indicates potassium chloride pellet spectra.)			
1	KCl	W-4(6), & methylated	1800-1500
2	KCl	W-4(6) acid-washed (HCl)	1800-1500
3	KCl	W-4(6), methylated & acid washed	1800-1500
4	KCl	W-4(6), methylated	1800-1500
5	KCl (a)	W-4(6), methylated	1800-1750
	(b)	then hydrolysed with NaOH	
	(c)	then reacidified	
	(d)	W-4(6), acid-washed	
6	KCl	W-1(6), ground sample washed with HCl refluxed with NaHCO ₃ methylated	1800-1500
7	KCl	Methylations by Diazomethane: 1-240-122 thru 1-505-122	1800-1500
8	KCl	4-67-122 through 4-251-122 (all methylated)	1800-1500
9	KCl	5-67-122 through 5-323-122 (all methylated)	1800-1500
10	KCl	1-240-122 to 1-505-122 (methylated by diazomethane)	1800-1500
11	PAS	W-4(6), & methylated	3100-2800
12	PAS	W-16(33), & methylated	3100-2800
13	PAS	W-4(6), & demineralized	1800-1500

Fig. #	Type	Sample Description	Frequency range (cm ⁻¹)
14	PAS	W-4(6) & demineralized	1200-800
15	PAS	W-16(33) & W-4(6)	3200-2700
16	PAS	W-16(33), W-4(6)	1800-1500
17	PAS	W-16(33), & W-4(6), each methylated	1200-1000
18	PAS	W-4(6), & W-4(6) methylated	3200-2700
19	PAS	W-16(33) & W-7(33), each methylated	3050-2750
20	PAS	Methylated samples from coal 4: 4-0 thru 4-407-i22	1800-1500
21	PAS	Methylated samples from coal 5: 5-0 through	1800-1500
22	PAS	Methylations: W-16(33), W-4(6), W-16(33) after 286 h. oxidation @ 158 degrees	1800-1500
23	PAS	Methylations by diazomethane: 2-240-122 thru 2-505-122	1800-1500
24	PAS	Methylations by diazomethane: 3-240-122 thru 3-505-122	1800-1500
25	PAS	Methylated samples: W-16(33), W-7(33), W-10(27), W-14(29)	1800-1500
26	PAS	Methylated samples: W-16(33), W-2(24), W-4(6)	1800-1500
27	PAS	Methylated samples: W-16(33), W-2(24), W-4(6)	1800-1500
28	PAS	W-4 oxidized 24 h. @ 150C, then methylated.	1800-1500
29	PAS	W-4 oxidized 48 h. @ 150C, then methylated	1800-1500
30	PAS	W-4 oxidized 75 h. @ 150C, then methylated	1800-1500
31	PAS	W-16 oxidized 24 h. @ 150, then methylated	1800-1500
32	PAS	W-16 oxidized 75 h. @ 150C, then methylated	1800-1500
33	PAS	W-16 oxidized 96 h. @ 150C, then methylated	1800-1500

Fig. #	Type	Sample Description	Frequency range (cm ⁻¹)
34	PAS	W-16(33), & after 15, 20, 30, 90 min. & 16 h. infrared irradiation	3200-2700
35	PAS	W-16(33), & after 15, 20, 30, 90 min. & 16 h. infrared irradiation	1200-800





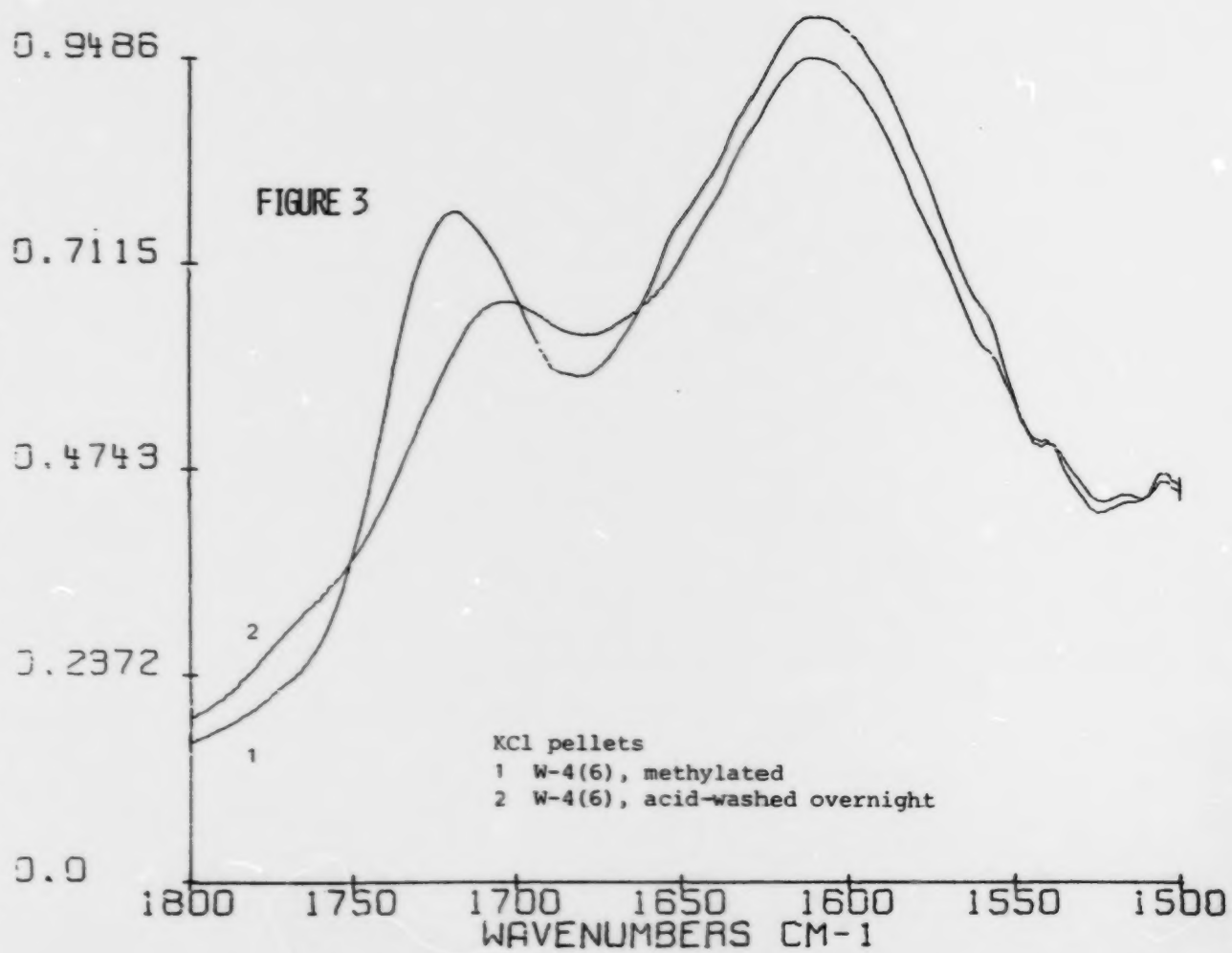


FIGURE 4

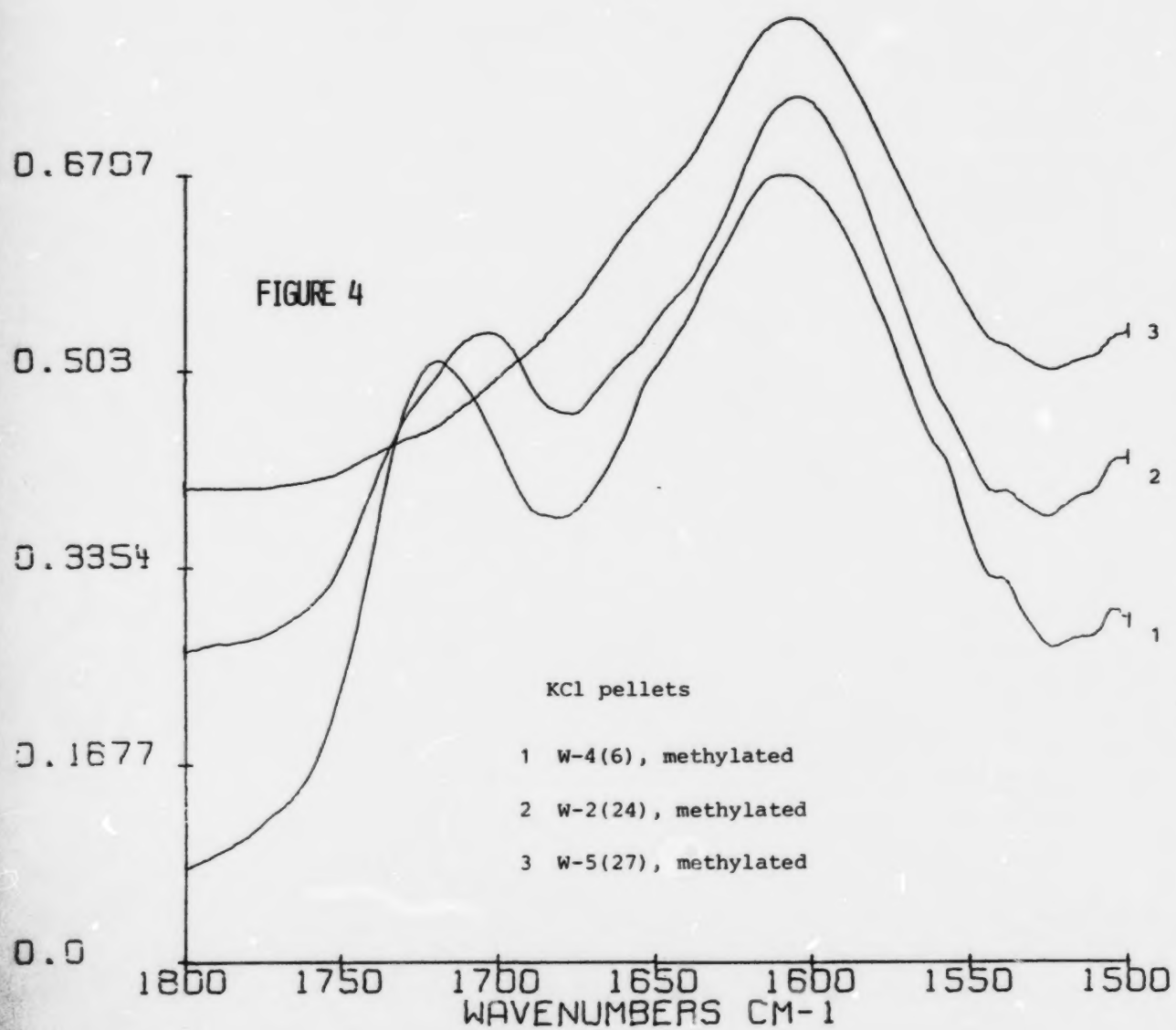


FIGURE 5

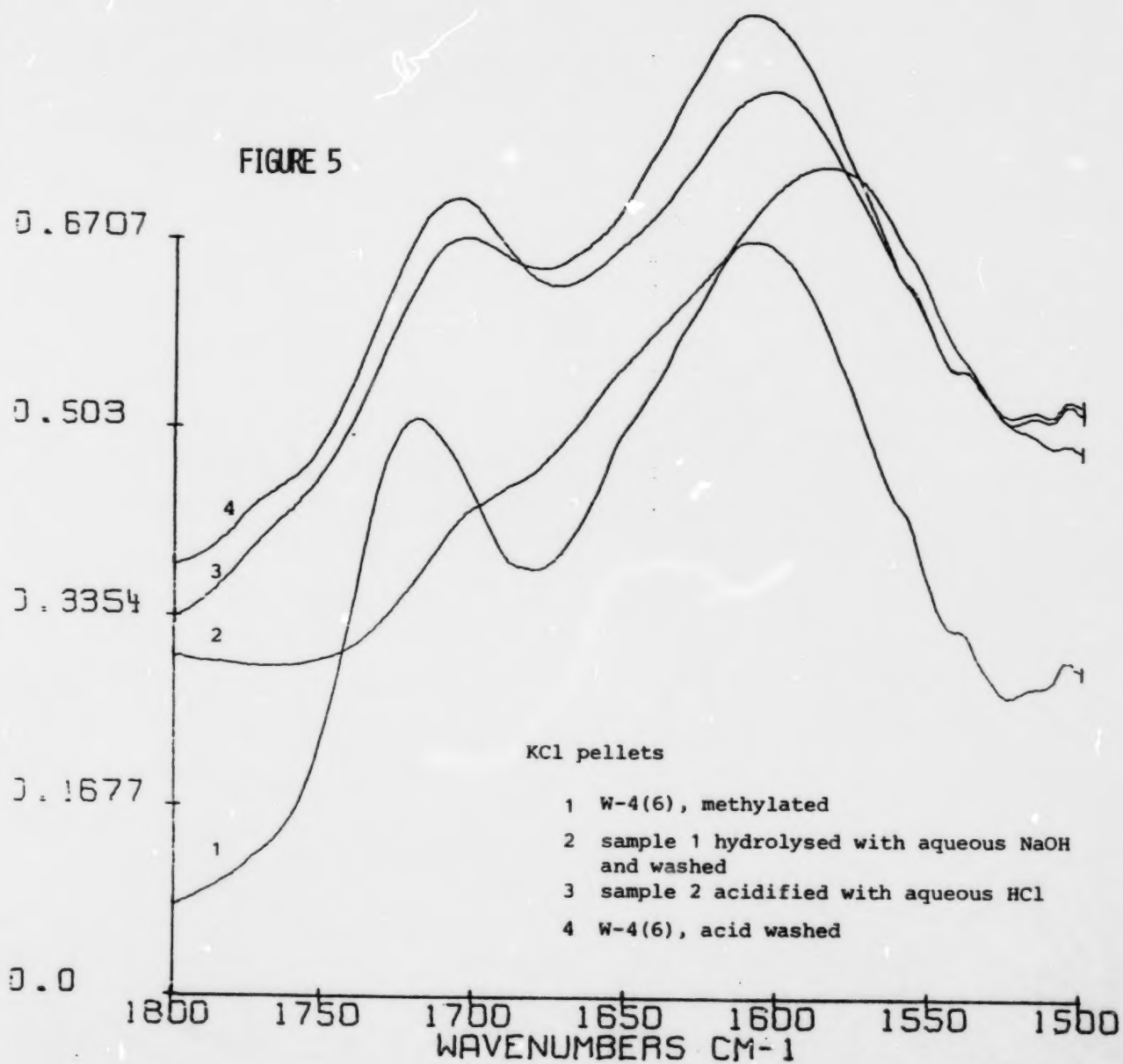


FIGURE 6

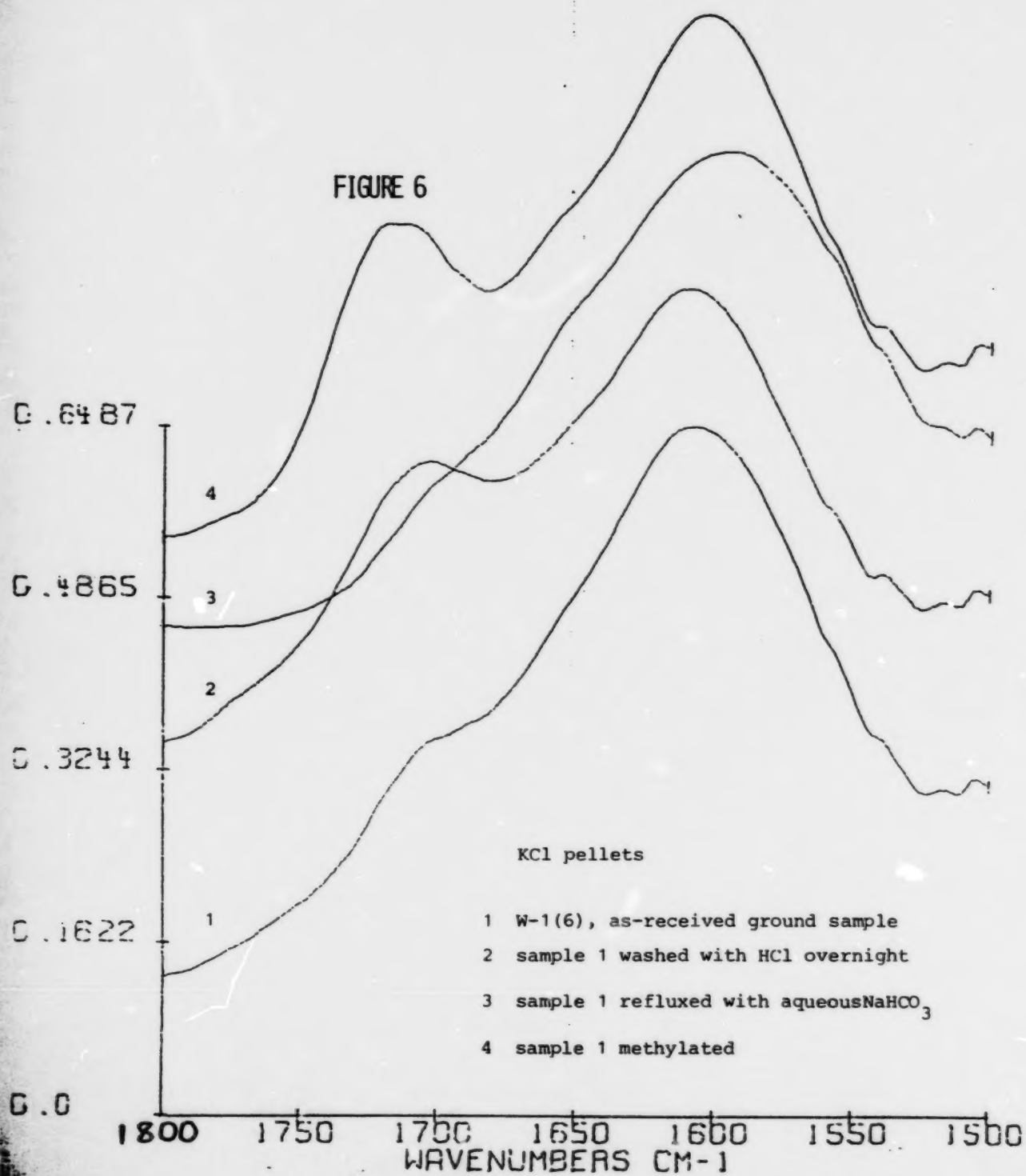


FIGURE 7

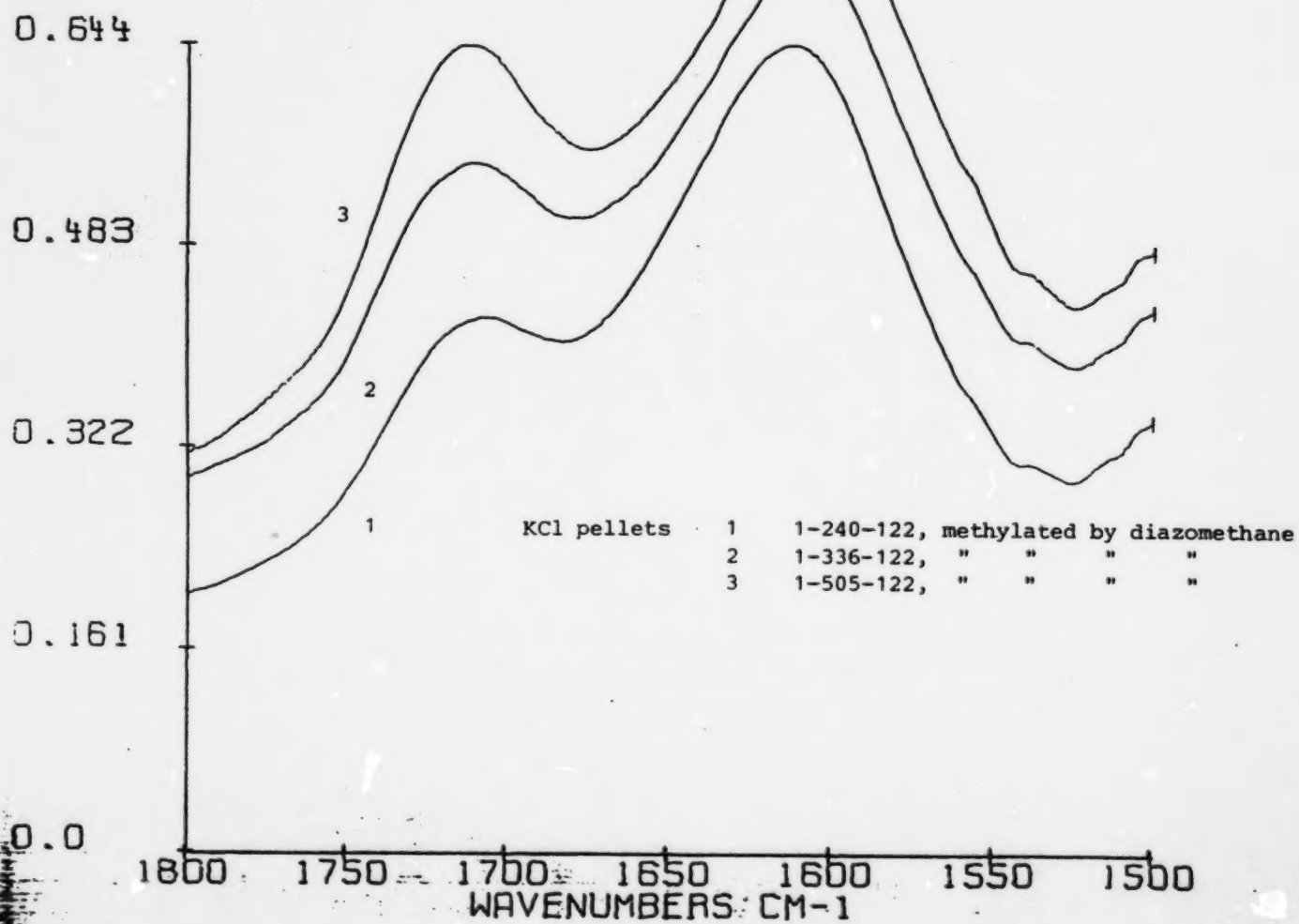
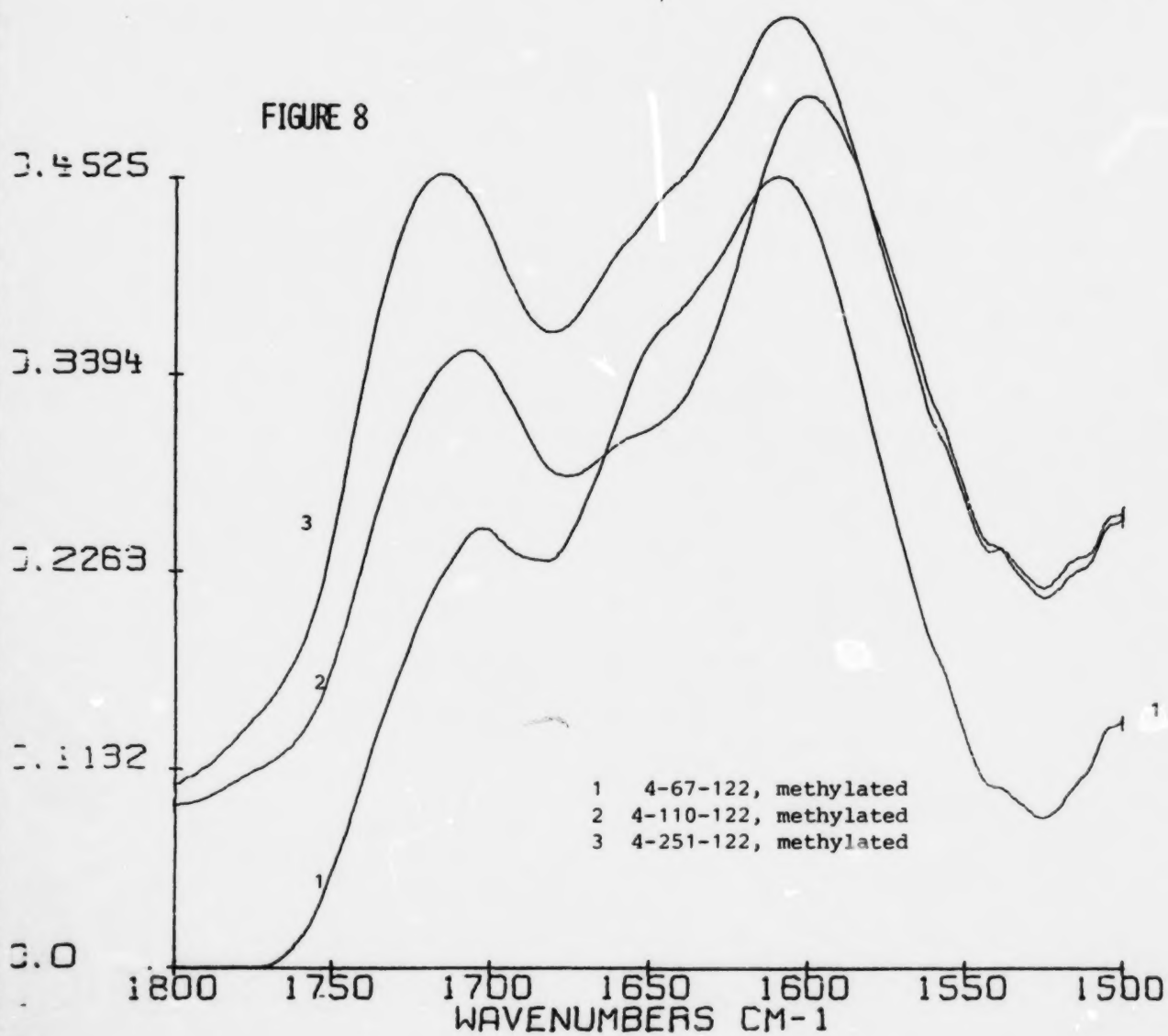


FIGURE 8



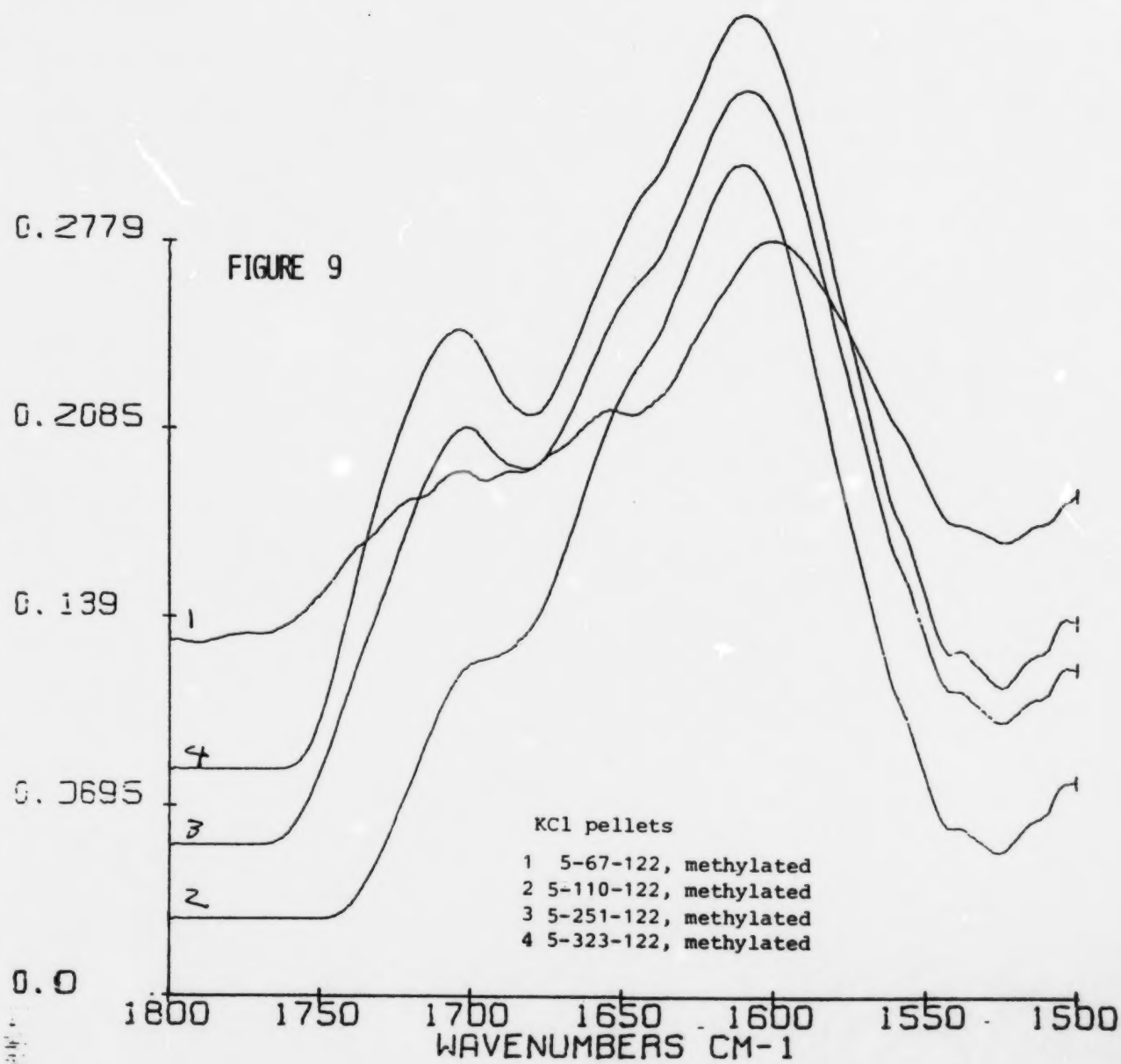


FIGURE 10

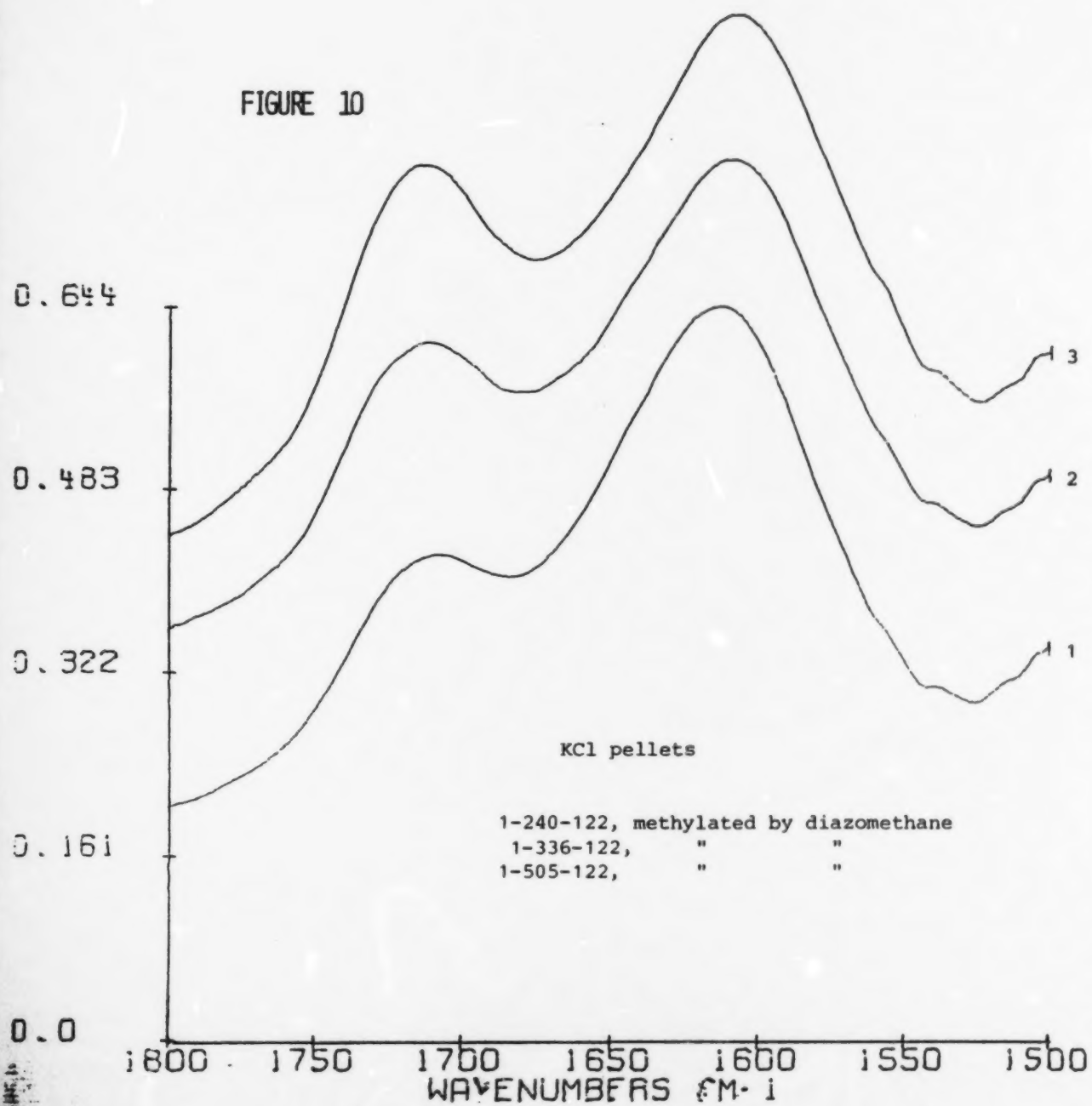
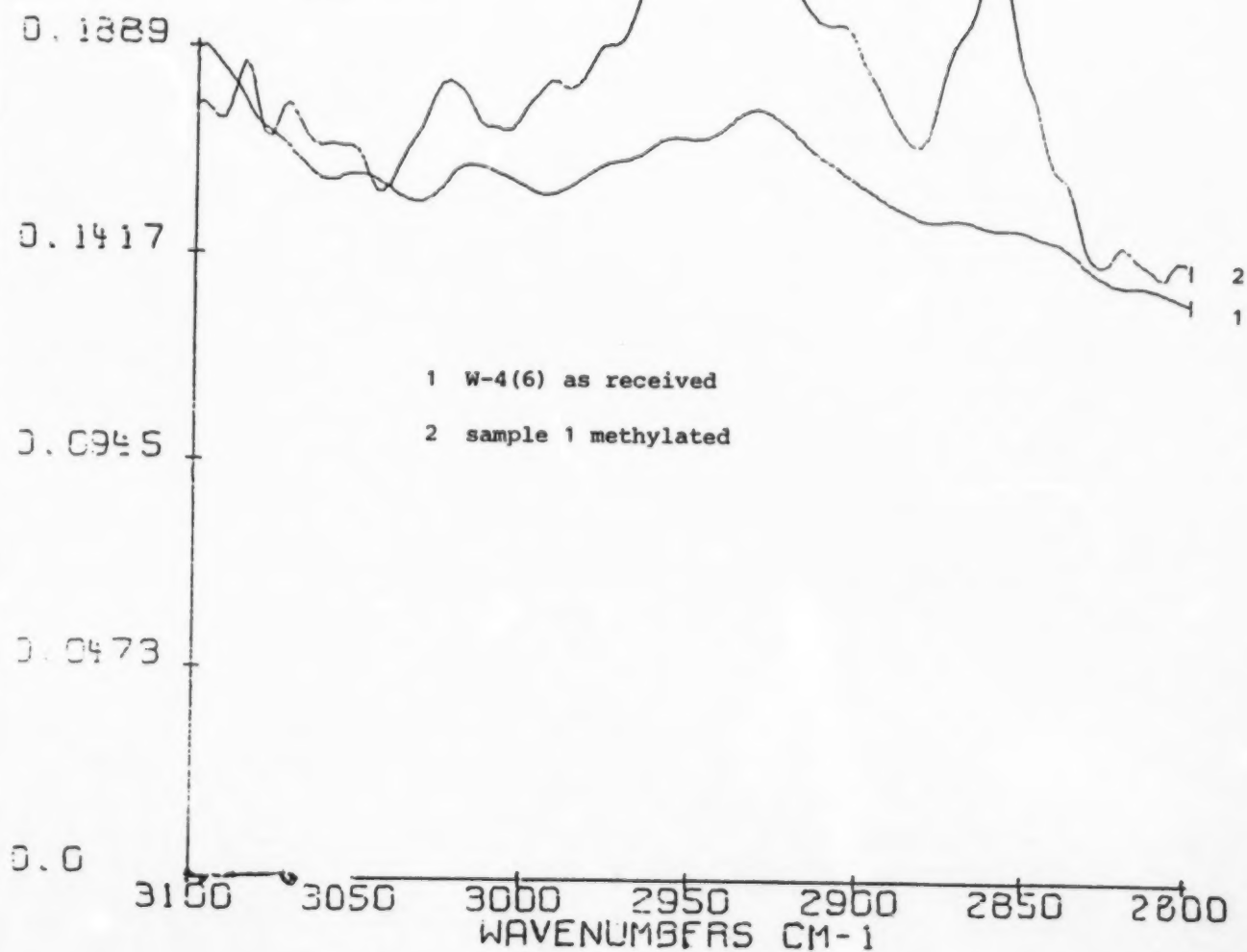


FIGURE 11



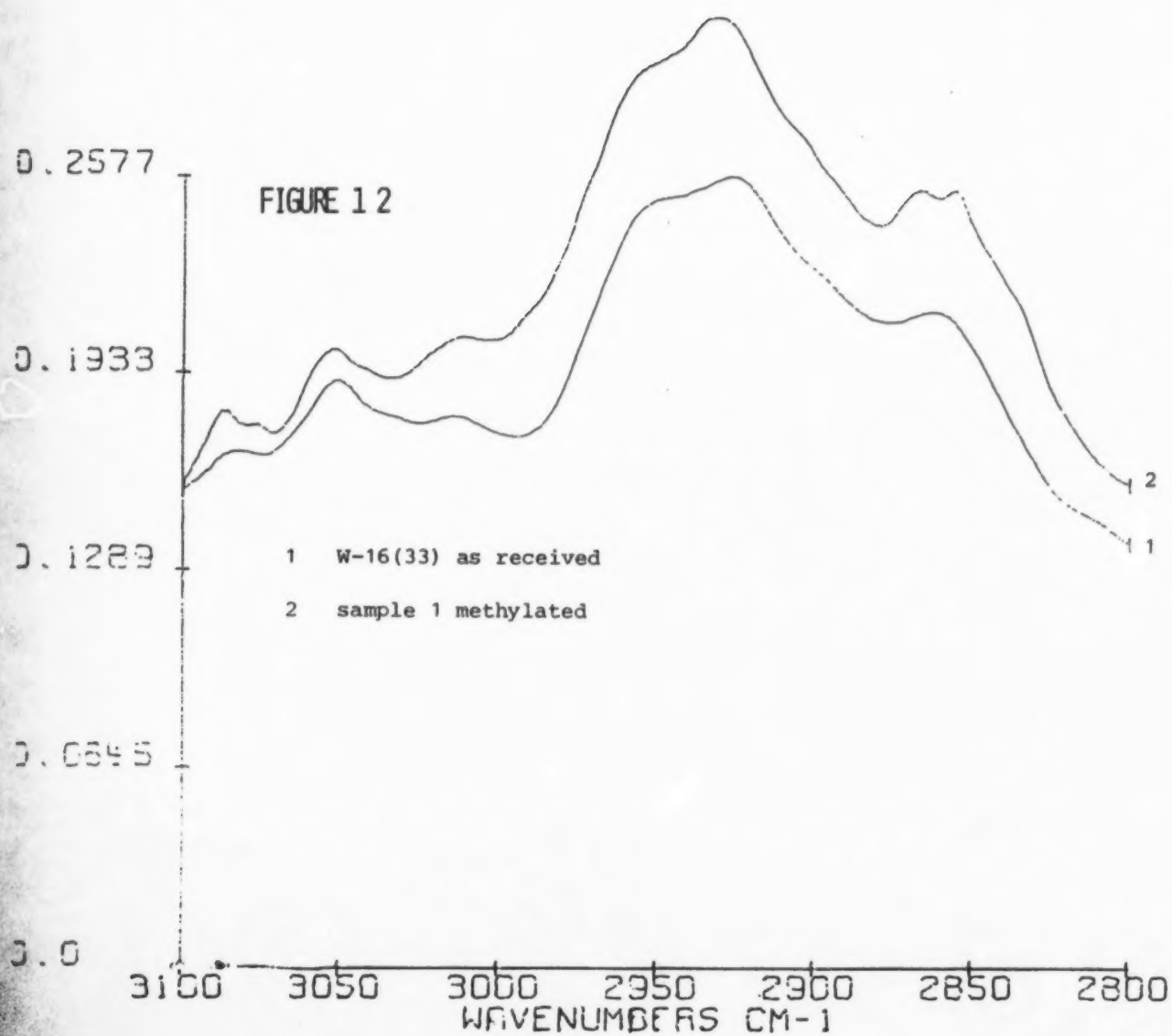


FIGURE 13

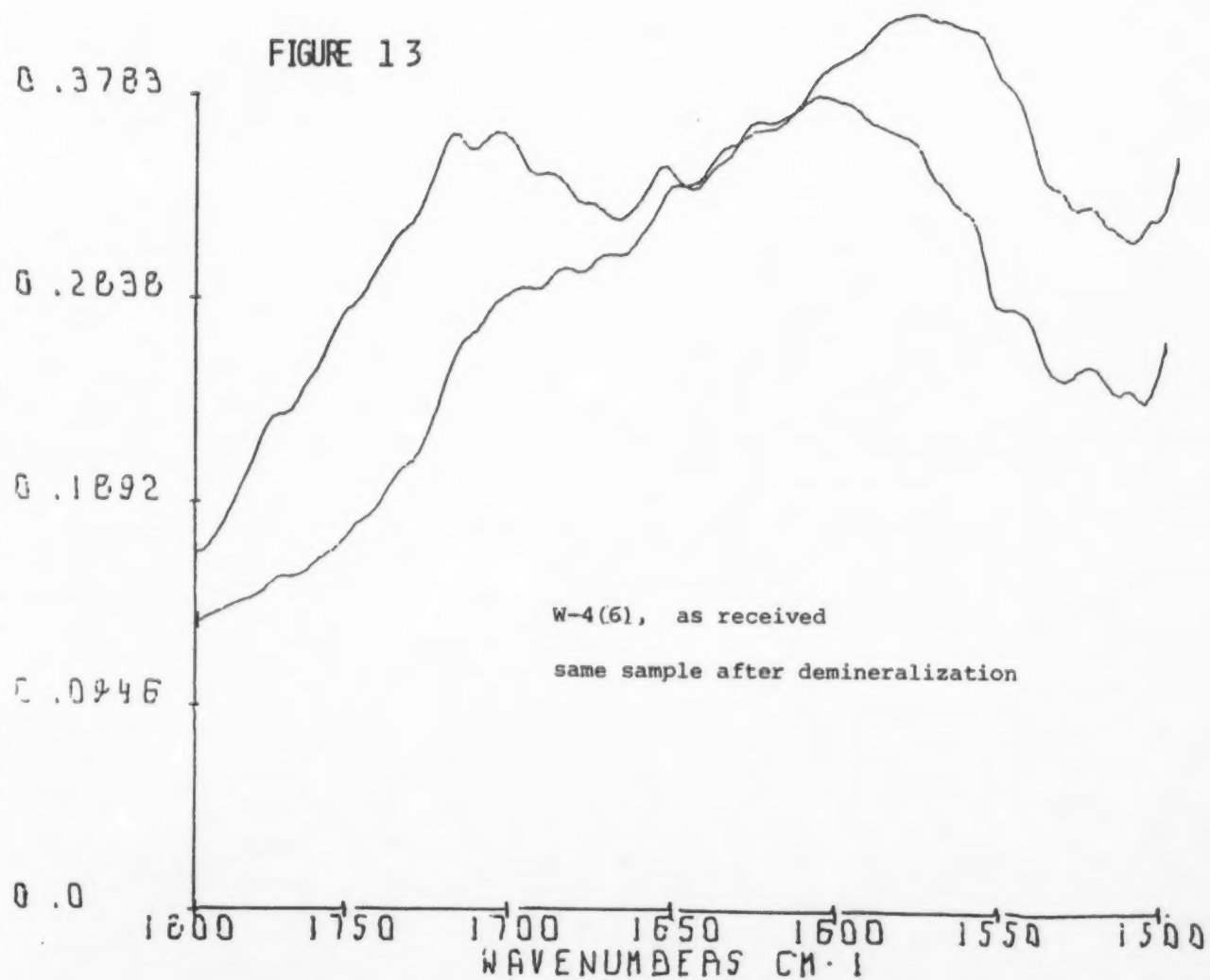


FIGURE 14

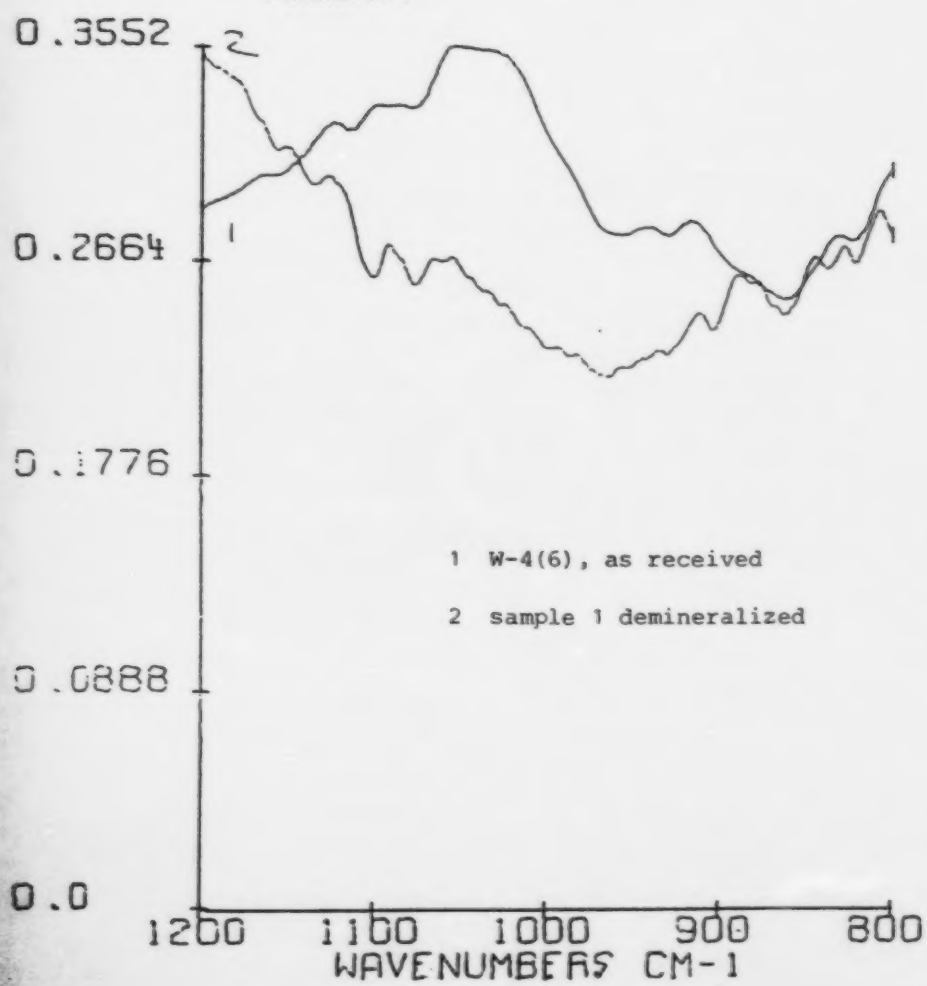
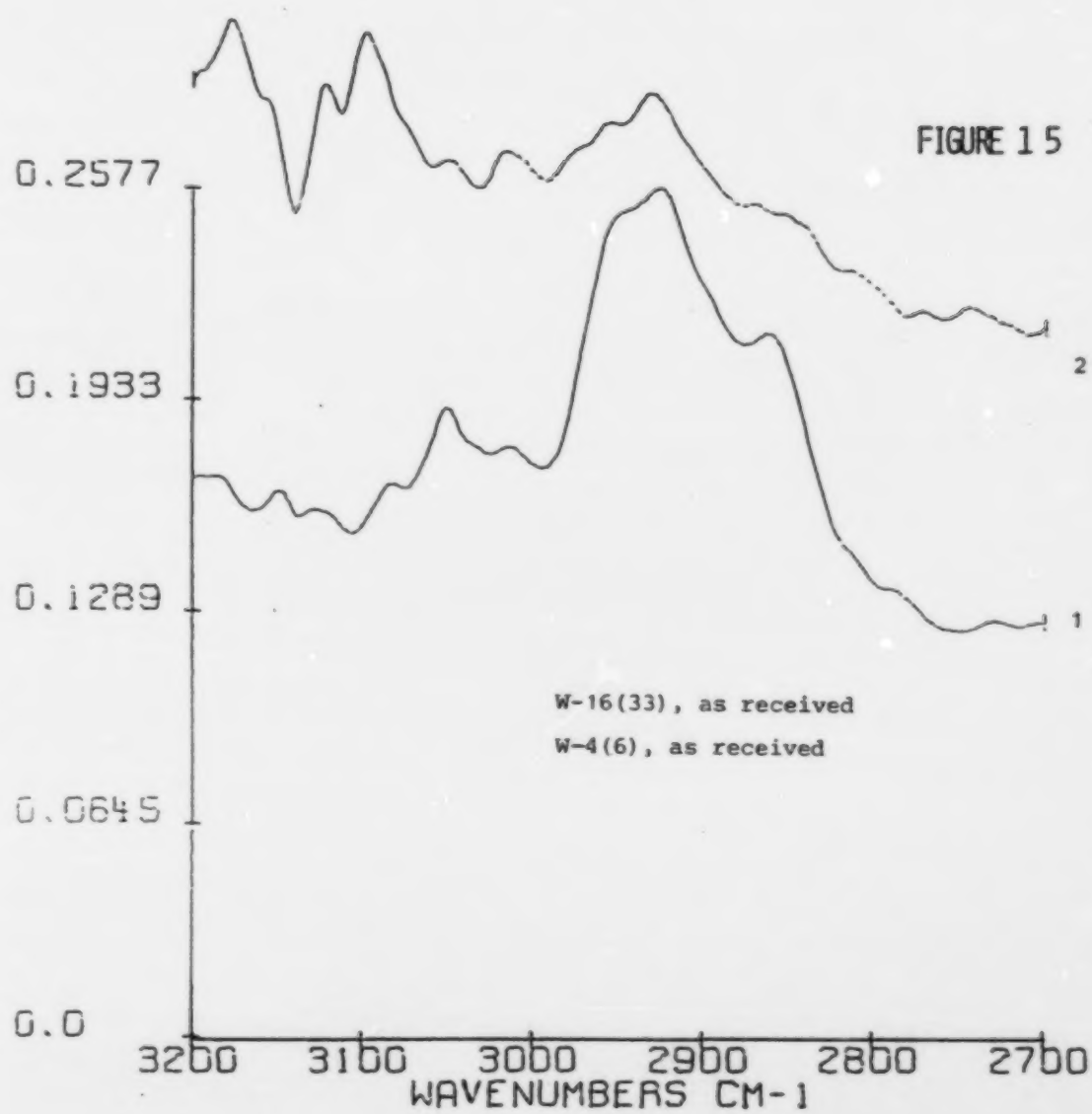
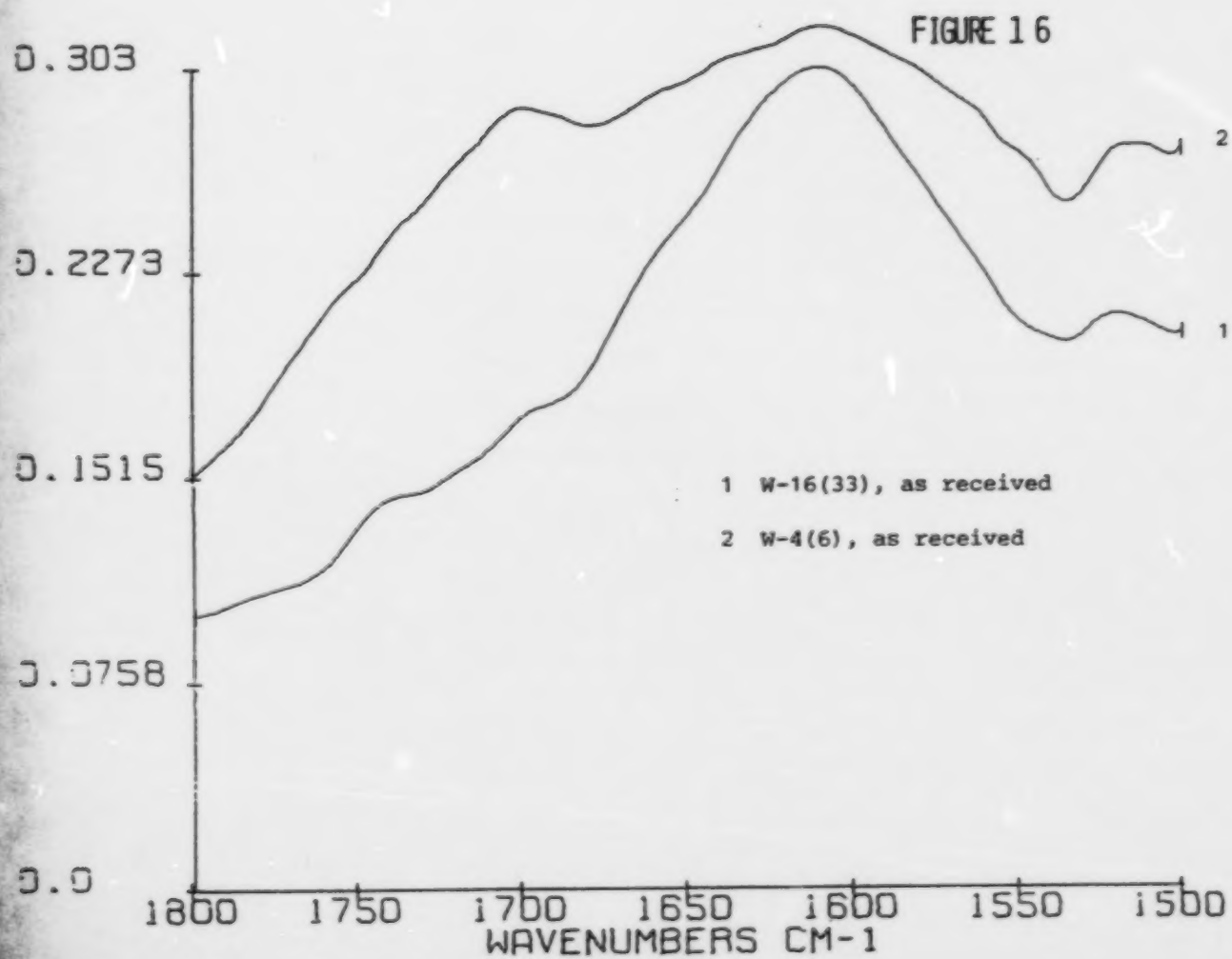


FIGURE 15





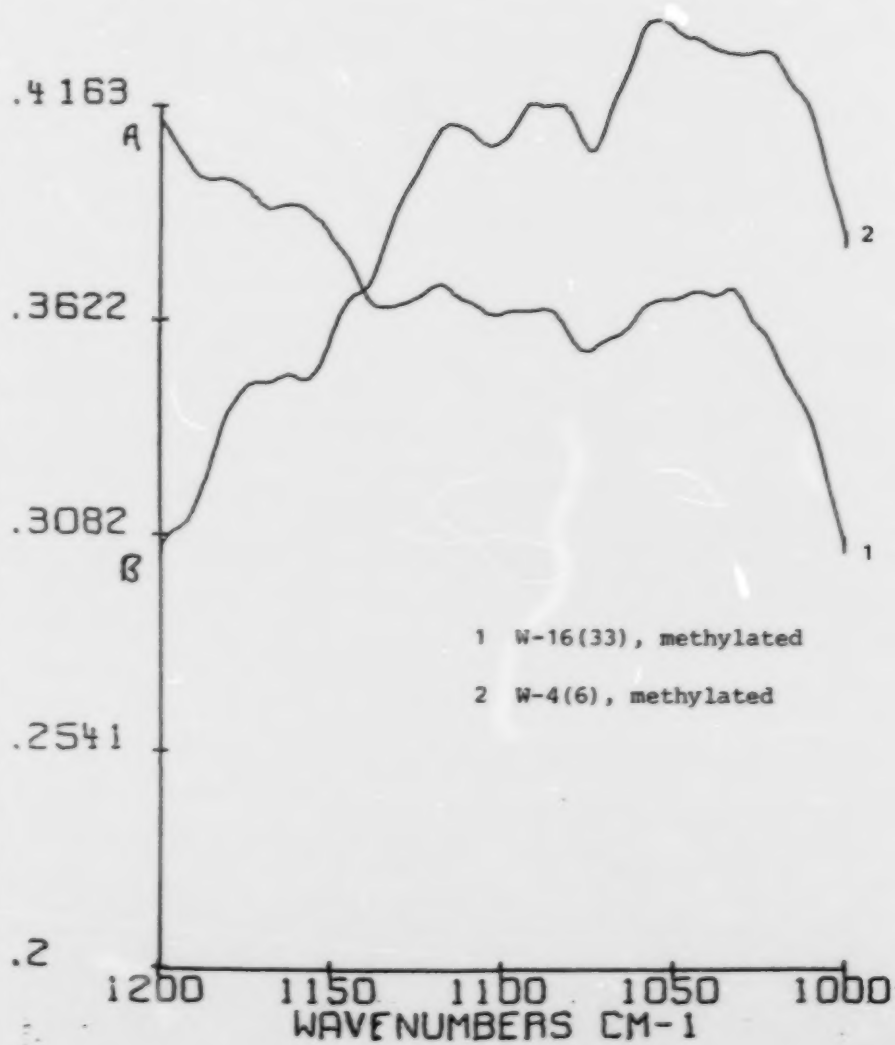


FIGURE 17

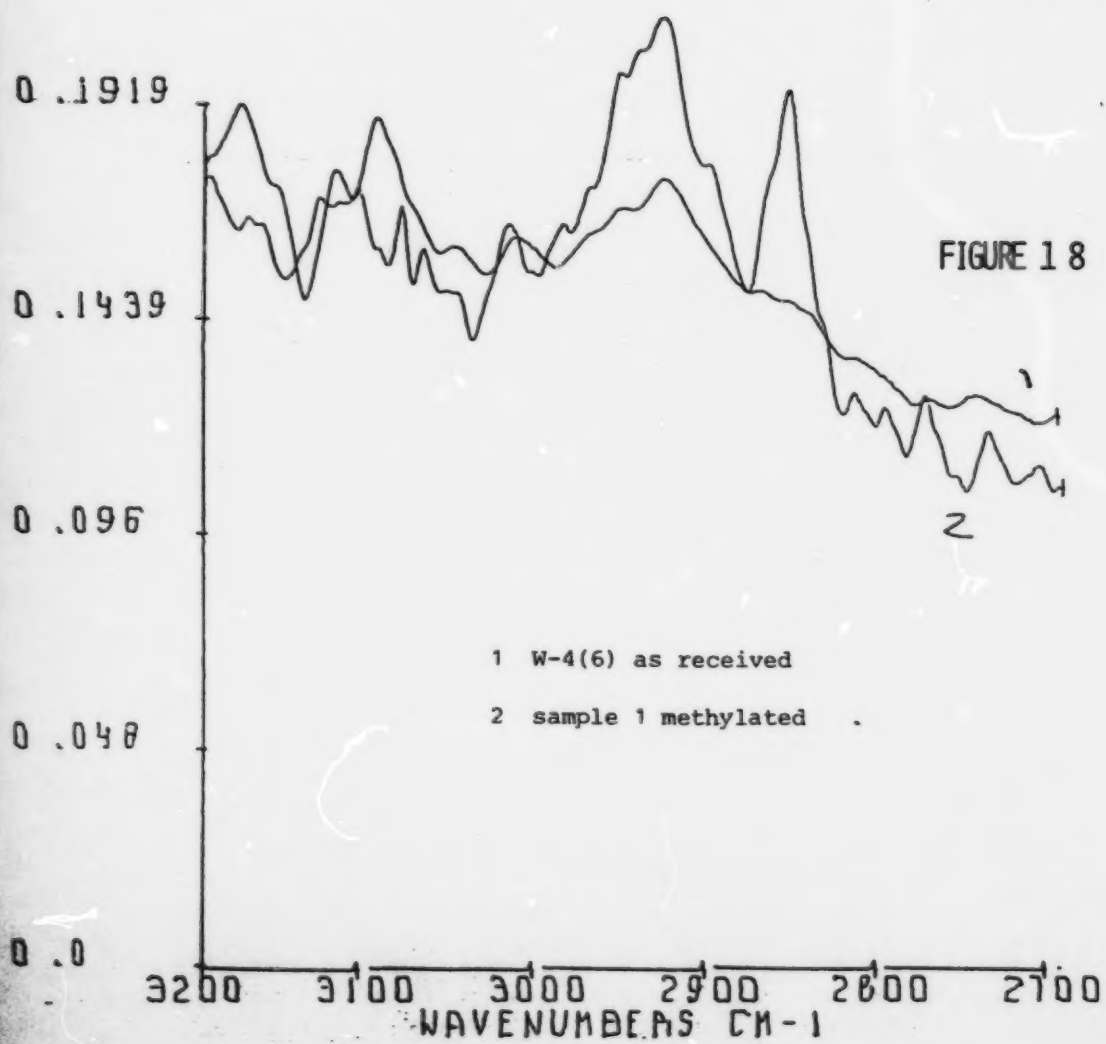


FIGURE 19

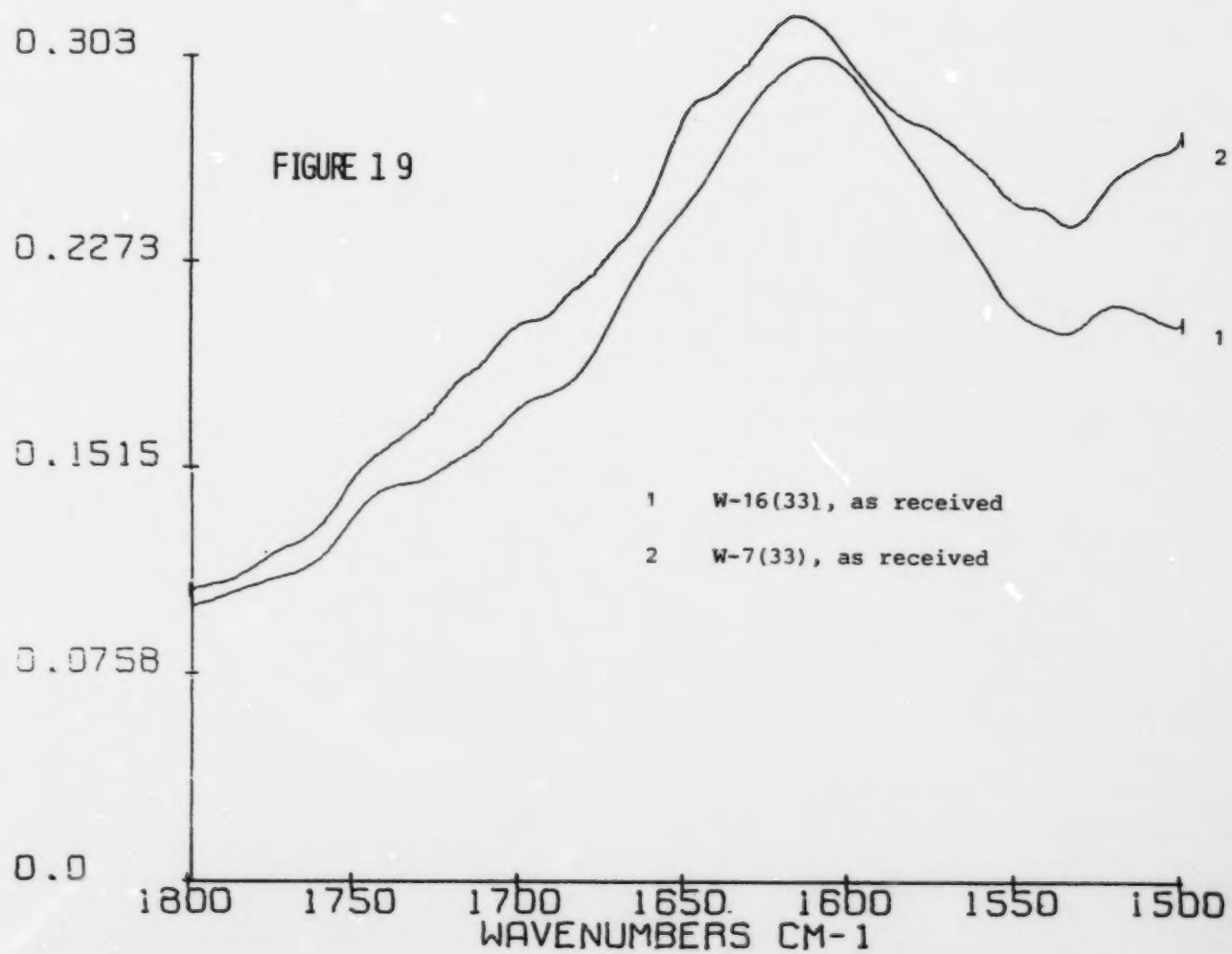


FIGURE 20

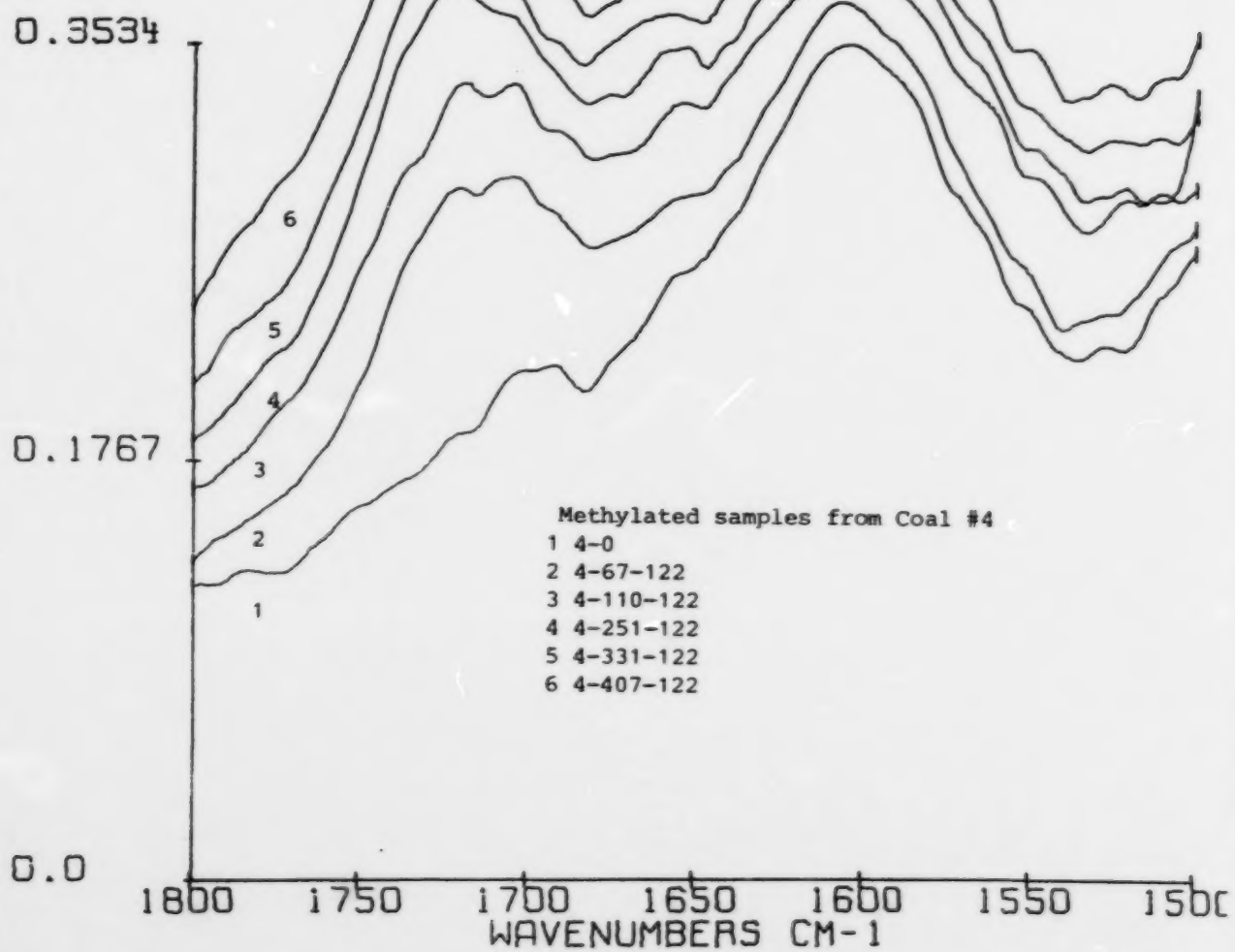


FIGURE 2 1

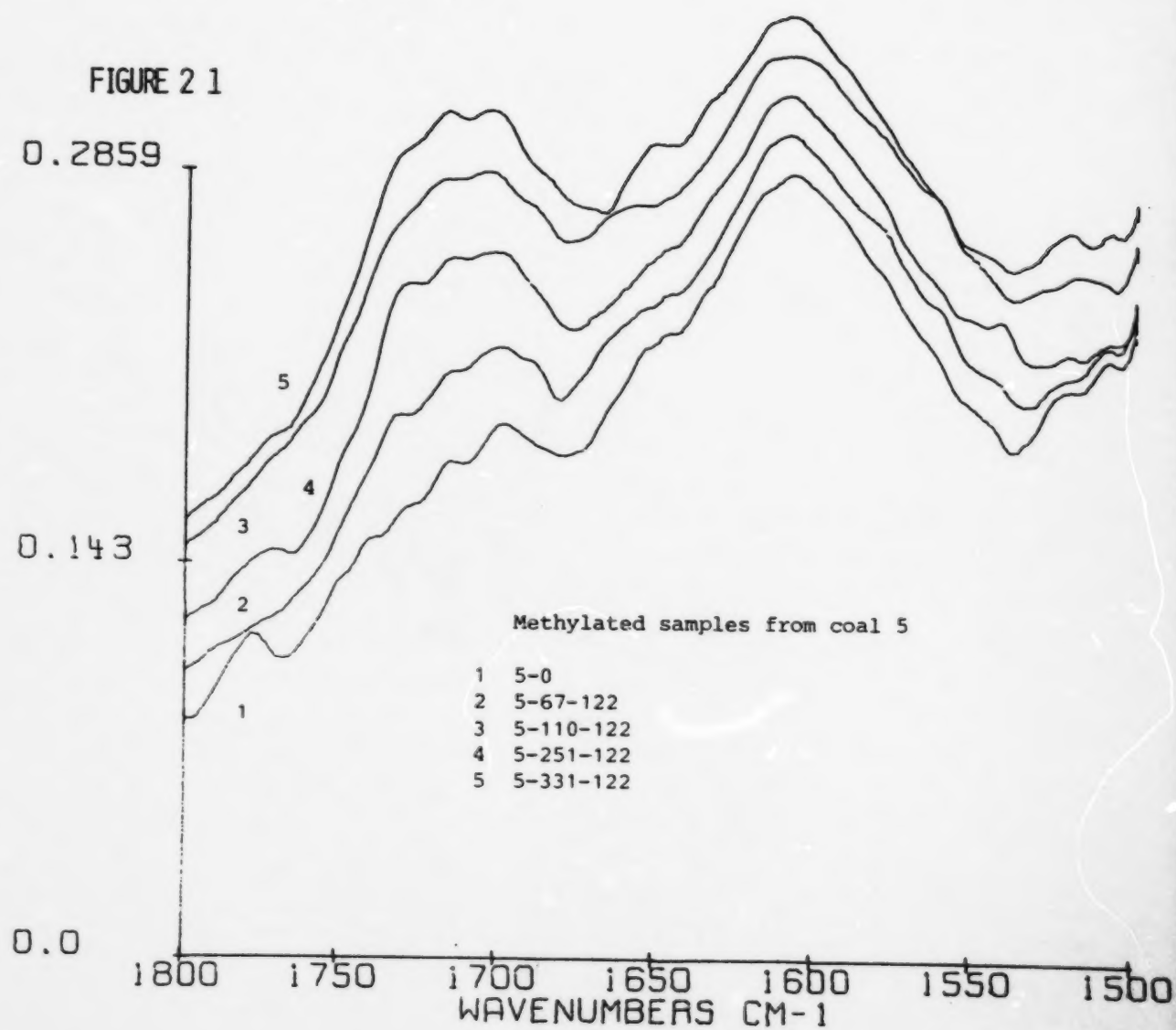


FIGURE 2 2

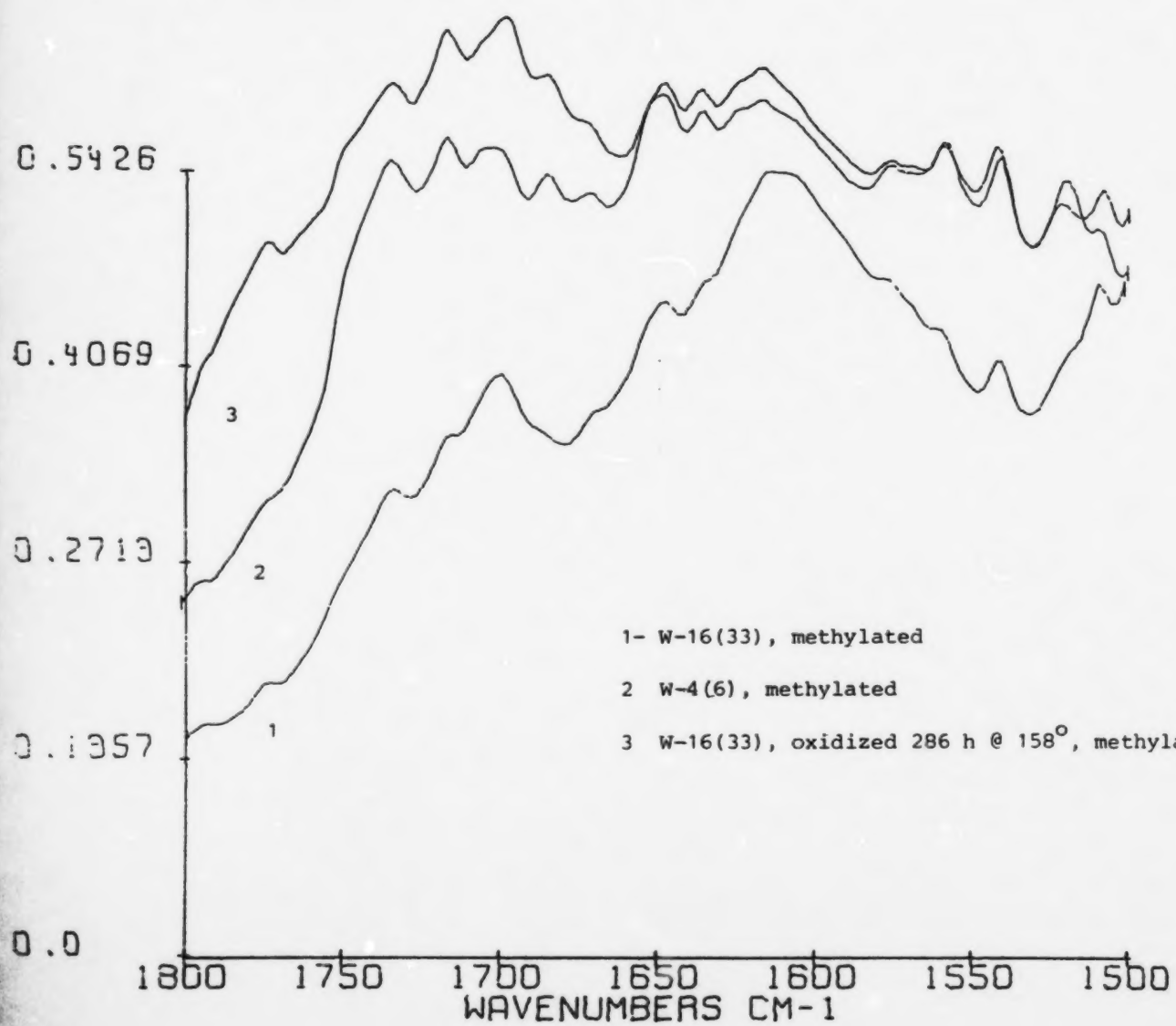


FIGURE 2 3

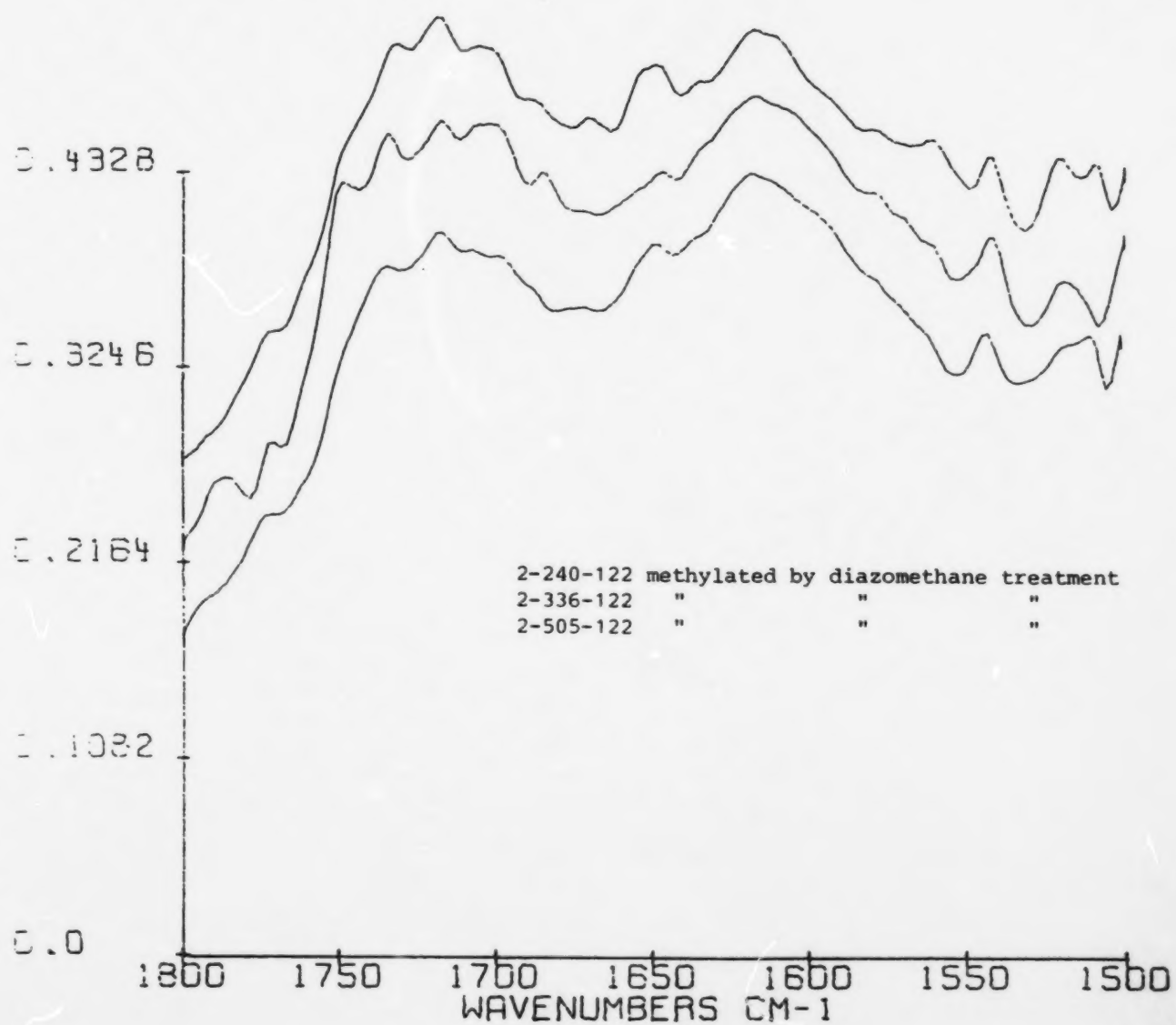


FIGURE 2 4

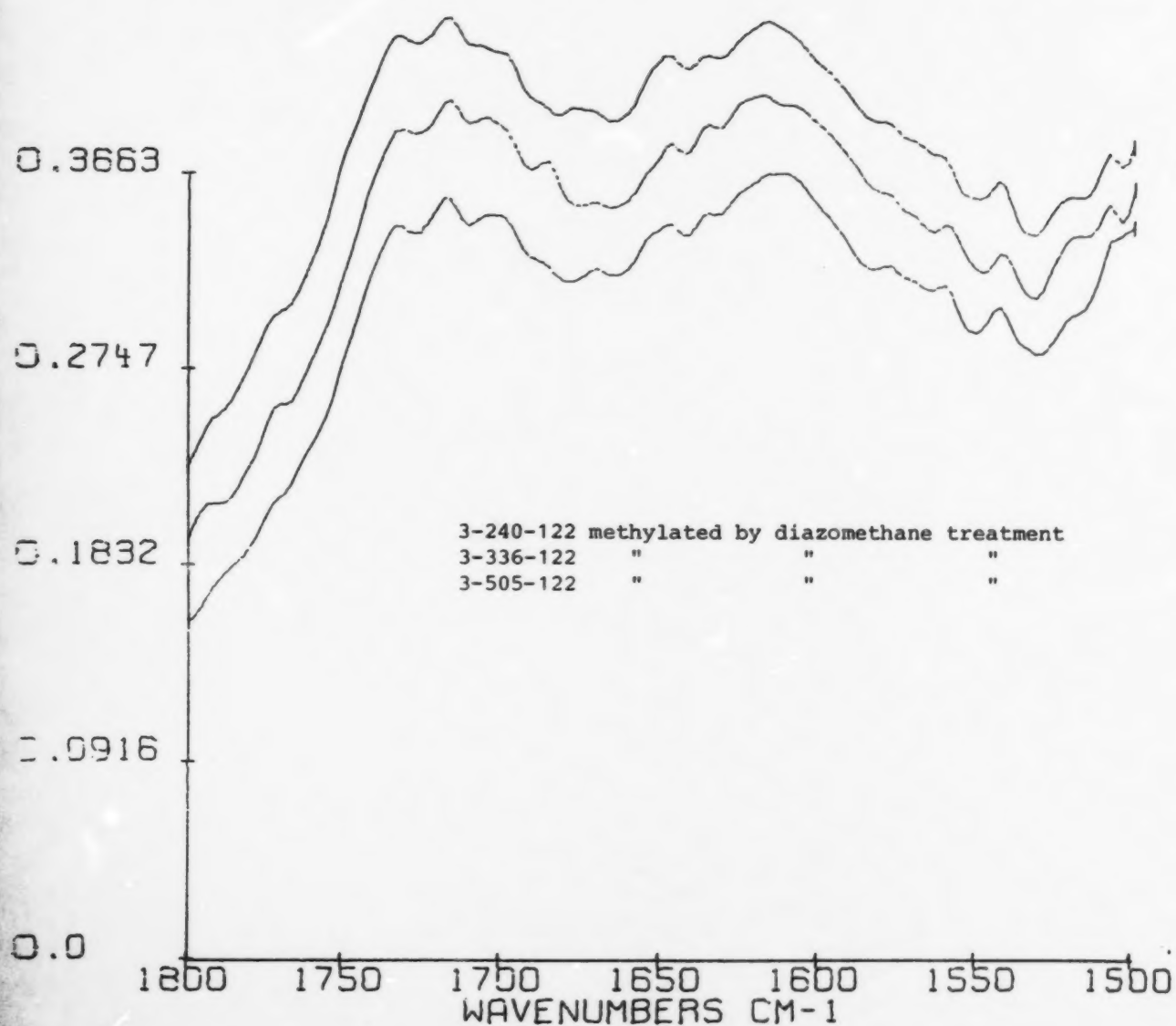


FIGURE 2 5

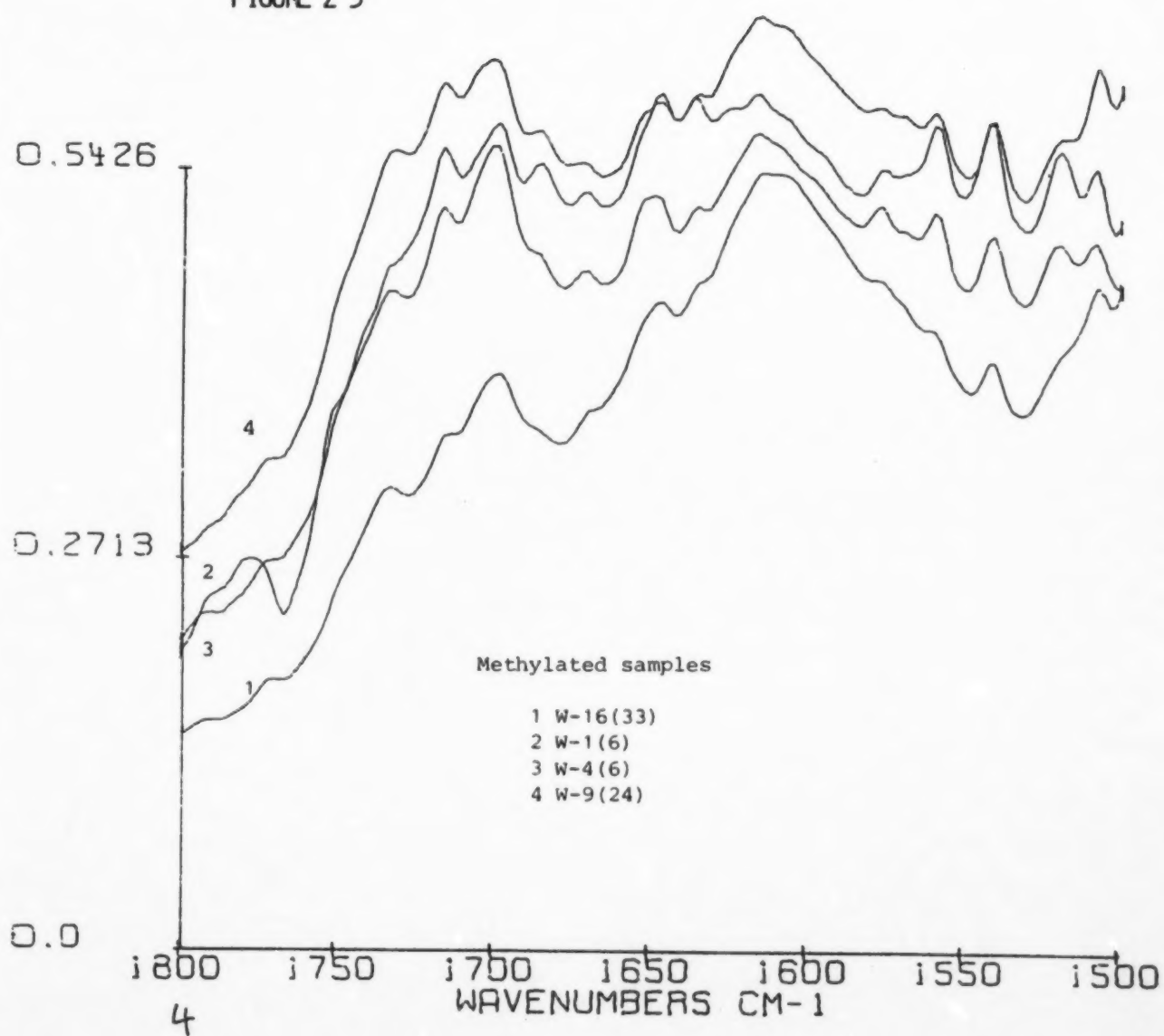


FIGURE 2 6

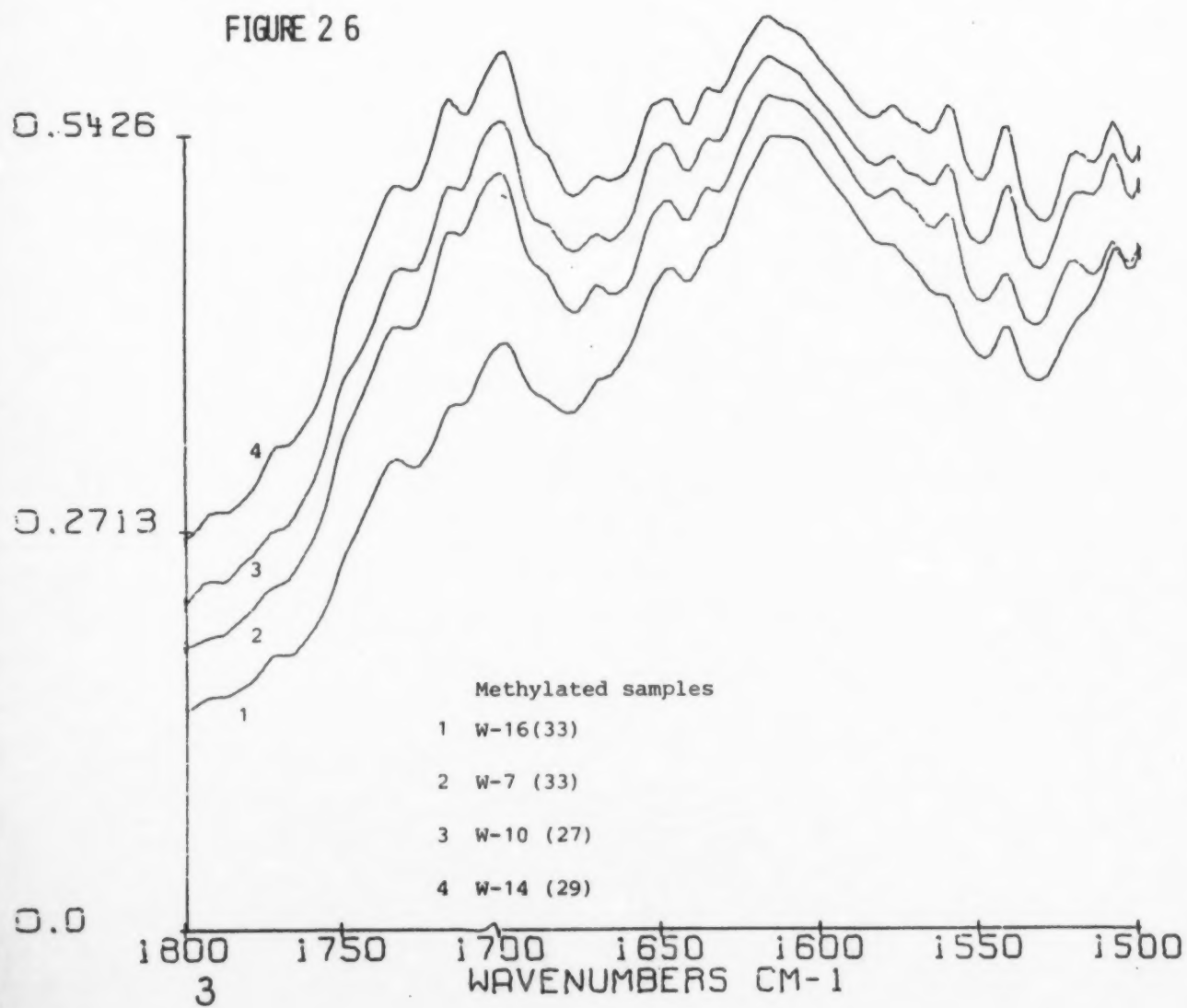


FIGURE 27

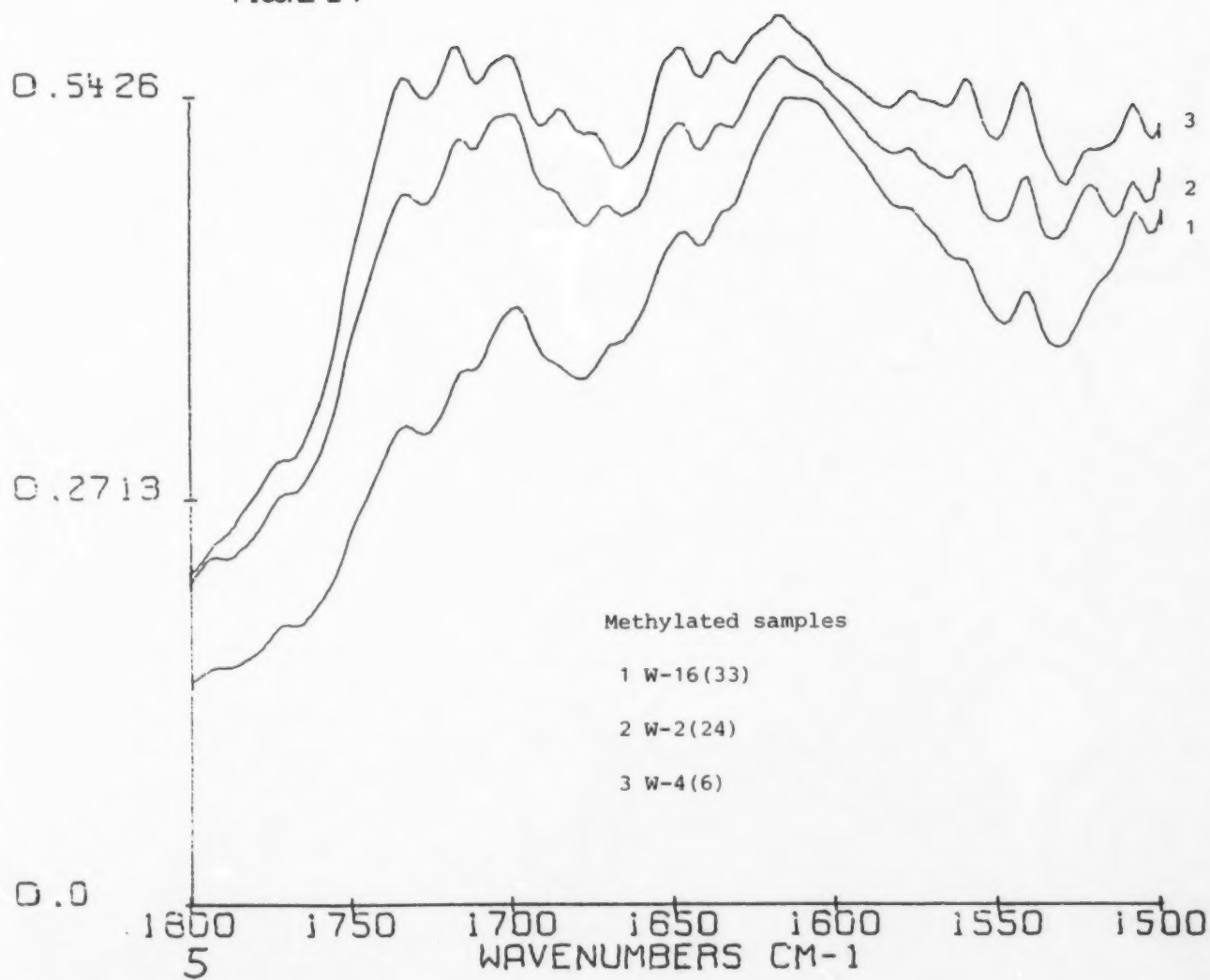


FIGURE 2 8

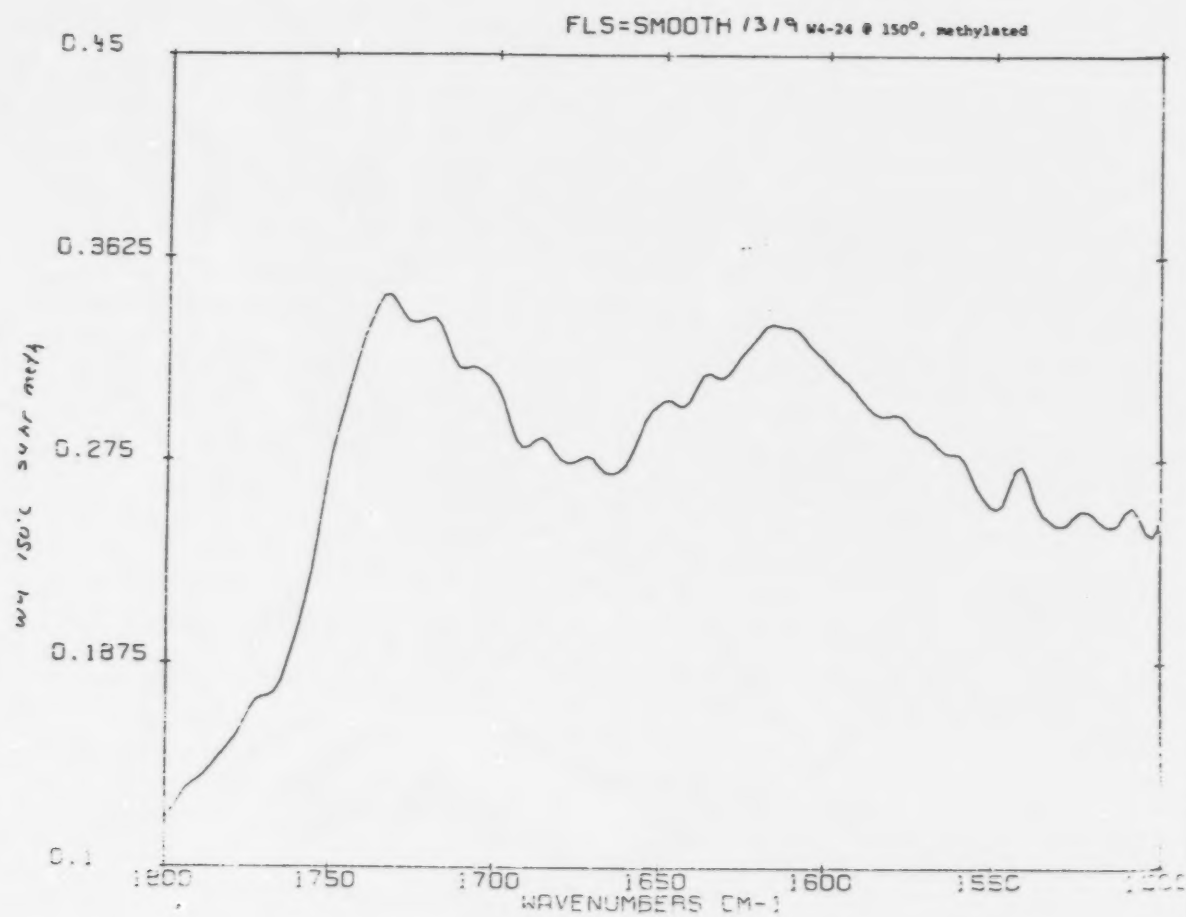


FIGURE 2 9

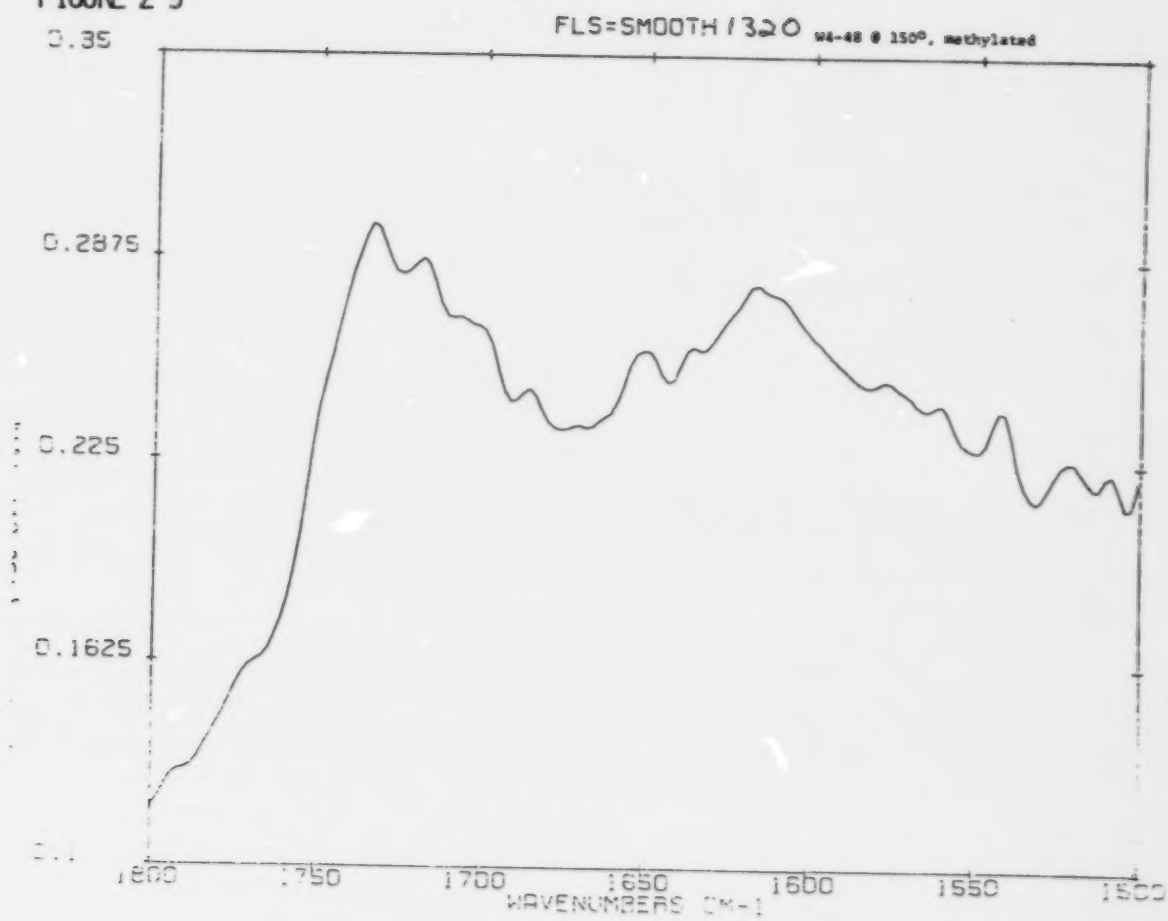


FIGURE 30

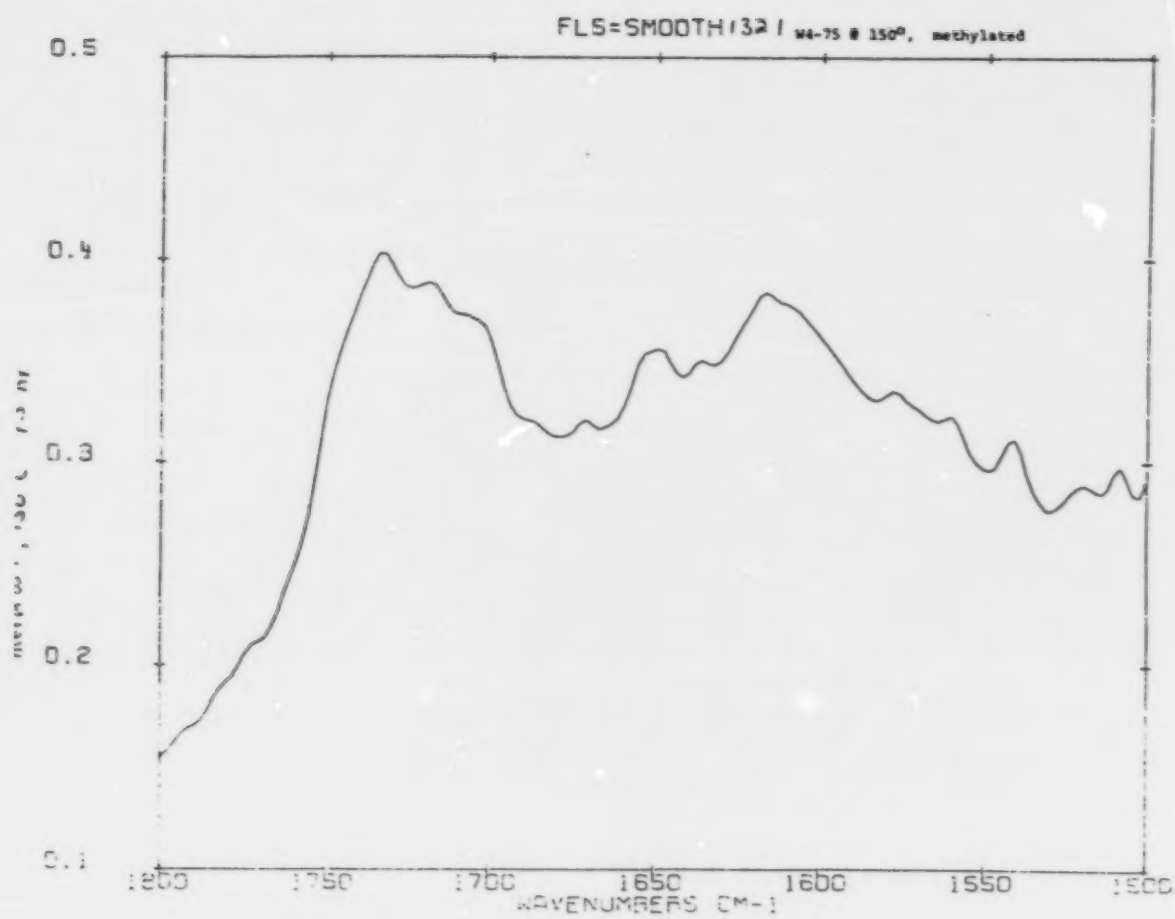


FIGURE 3 1

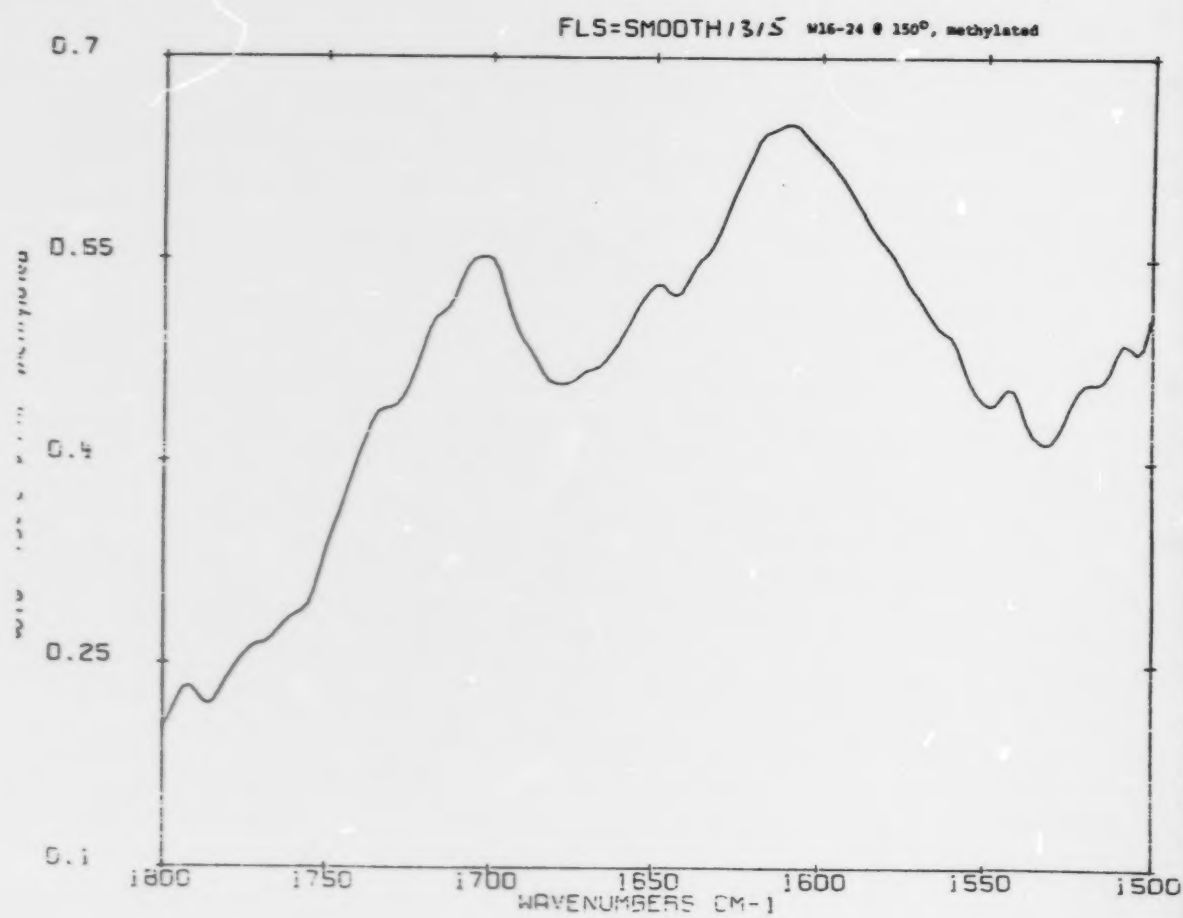


FIGURE 3 2

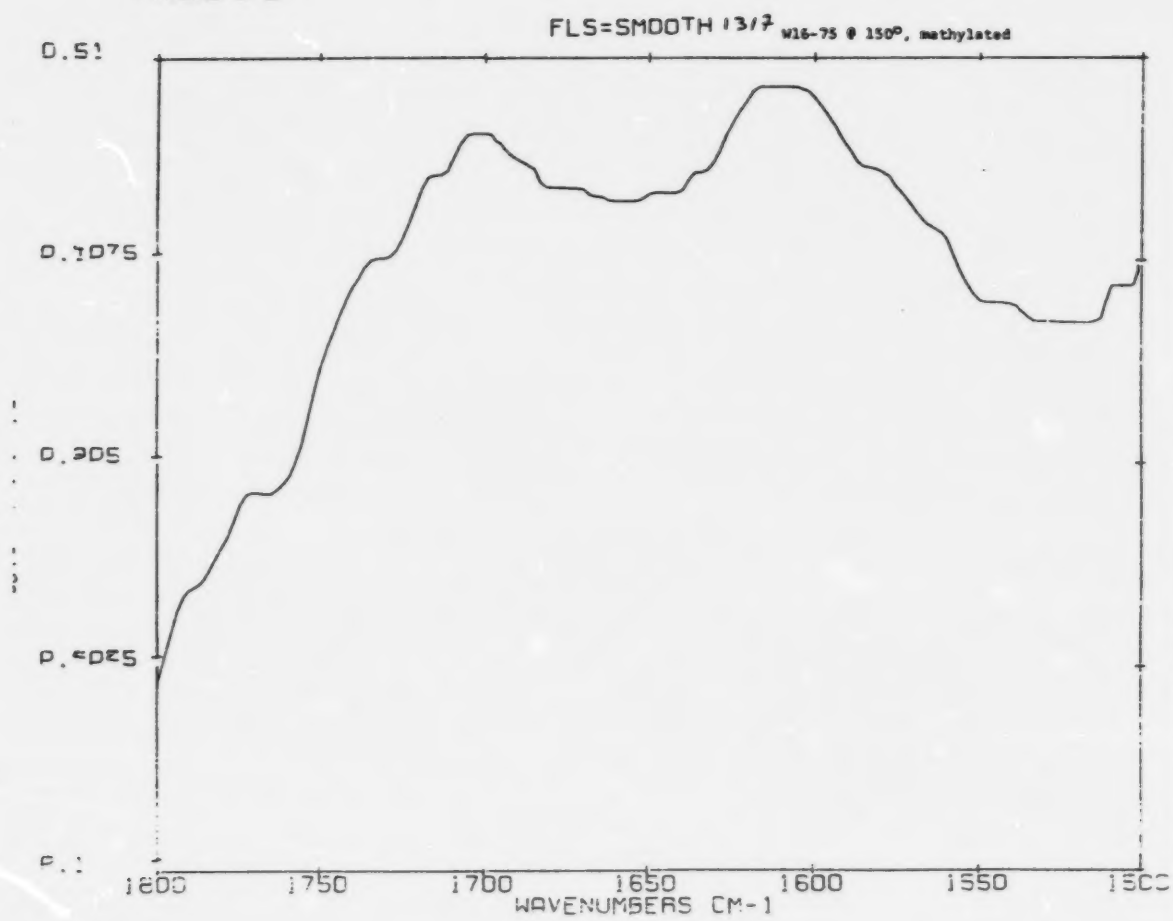


FIGURE 3 3

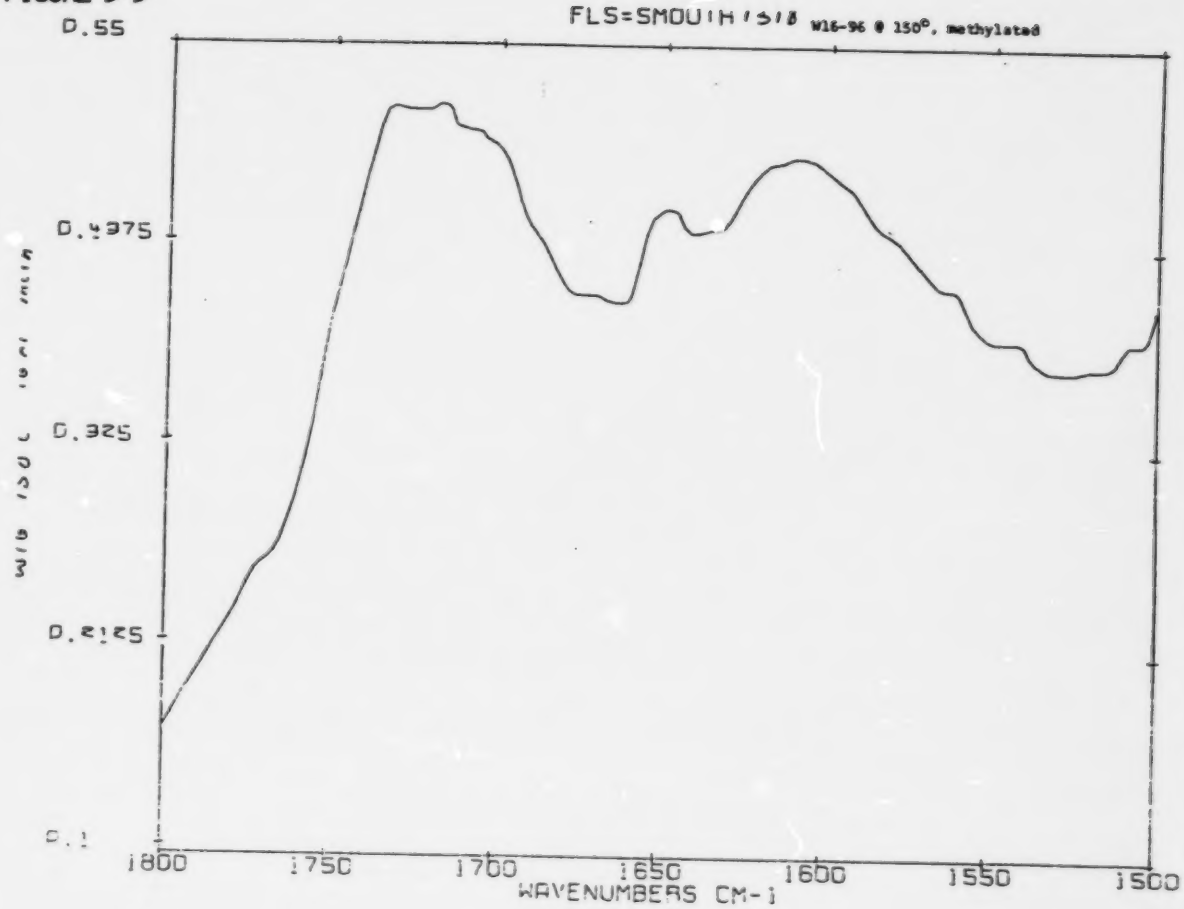


FIGURE 3 4

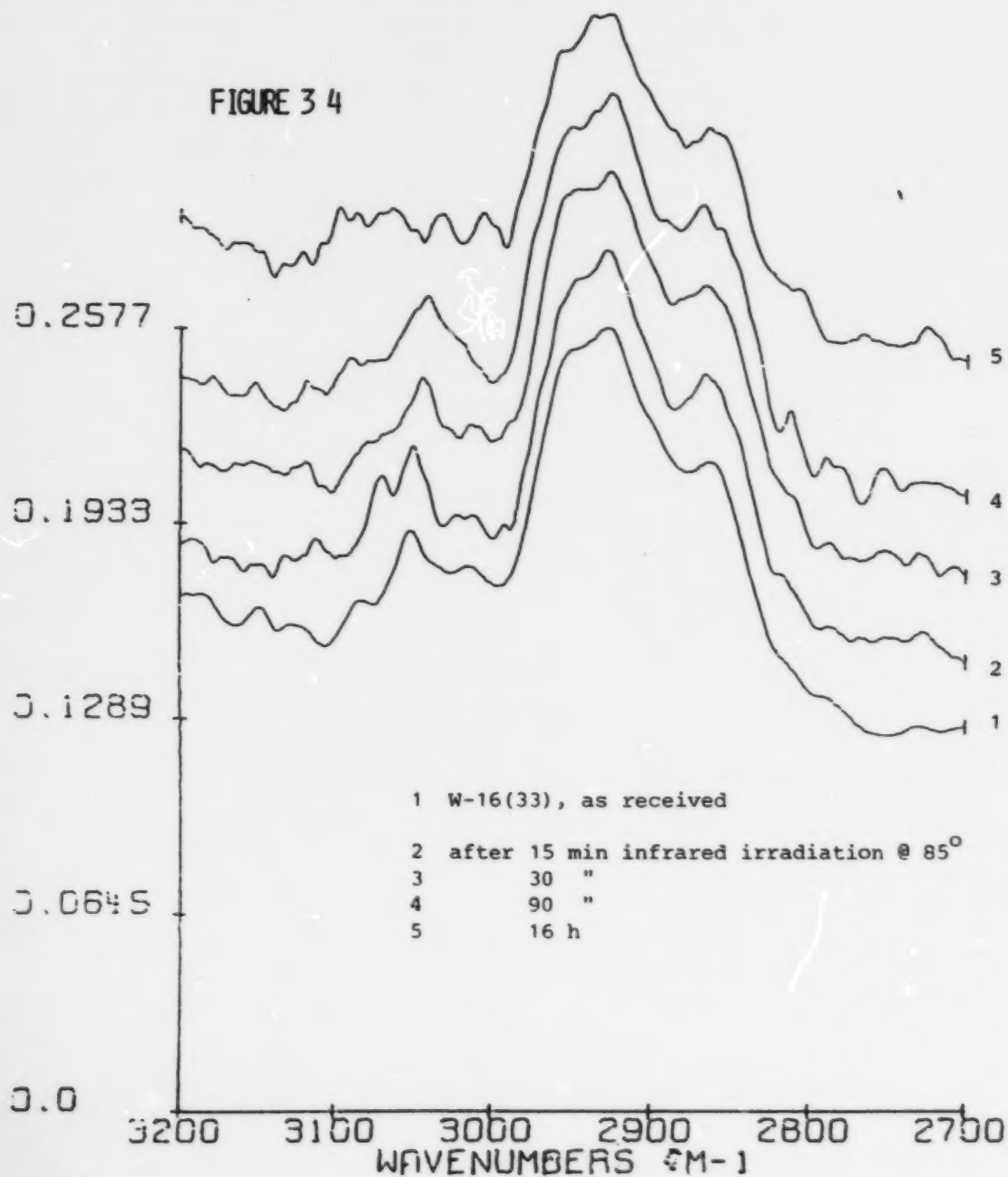


FIGURE 3 5

